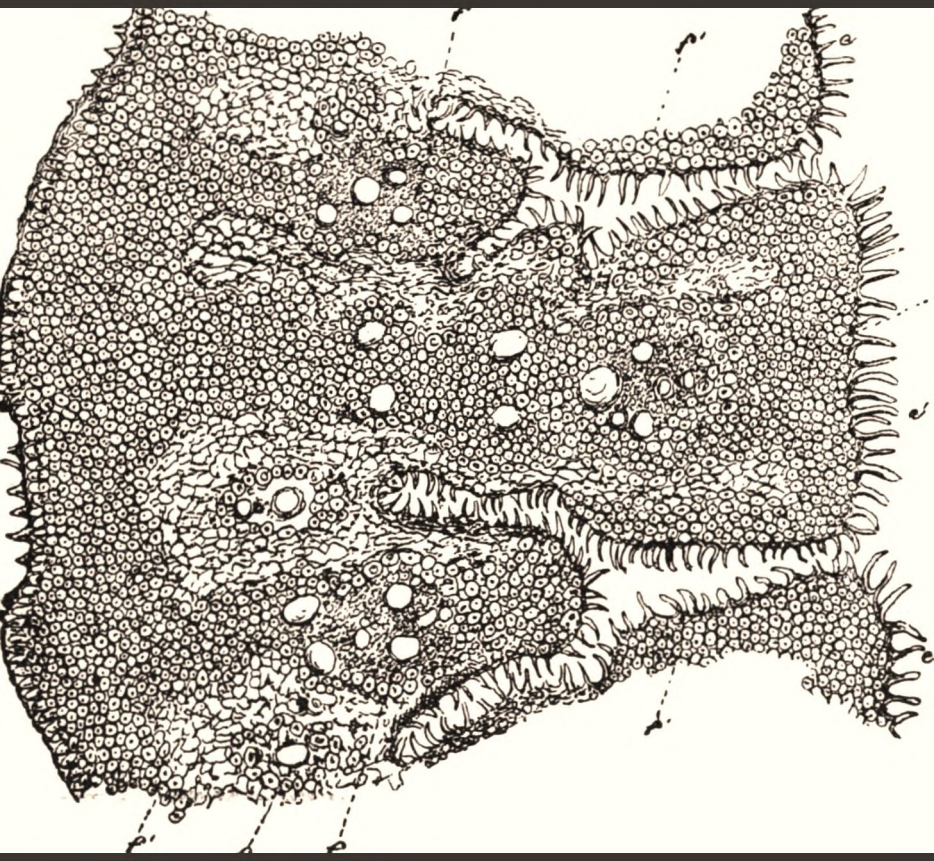

A text-book of paper-making

Charles Frederick Cross,
Edward John Bevan, J. F. Briggs

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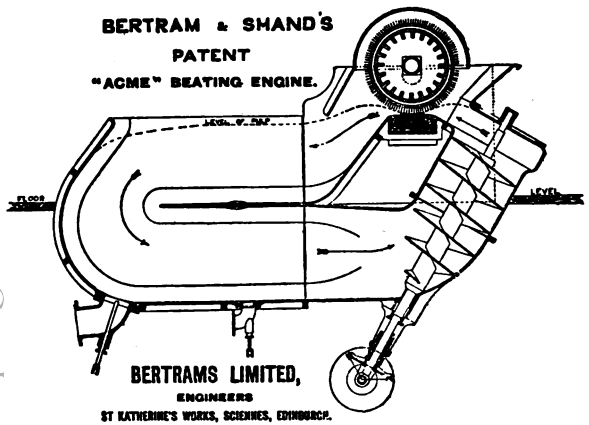

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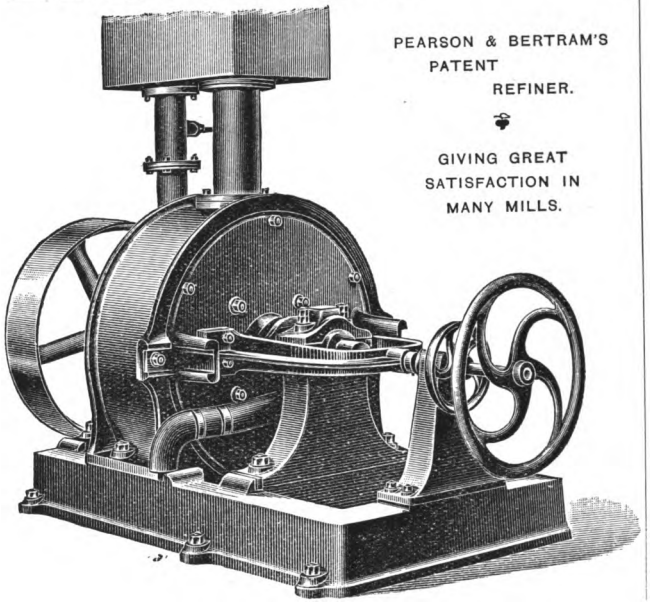

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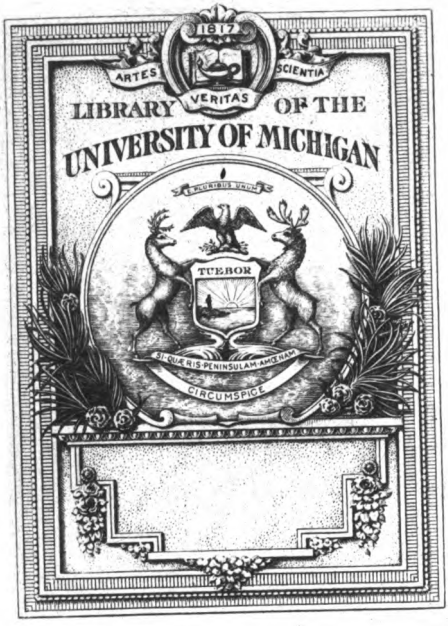

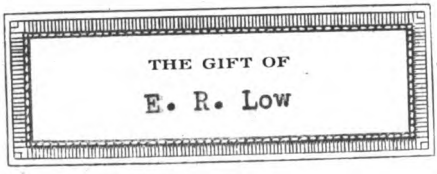

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OF

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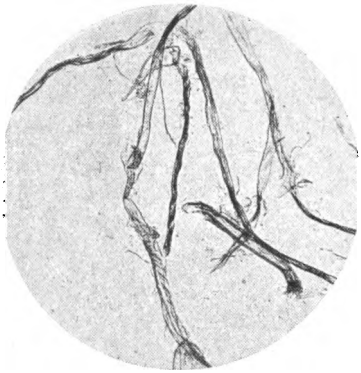
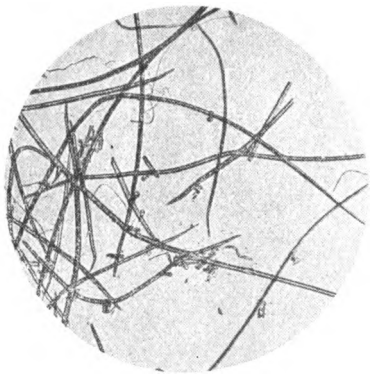


COTTON PULP

LINEN PULP



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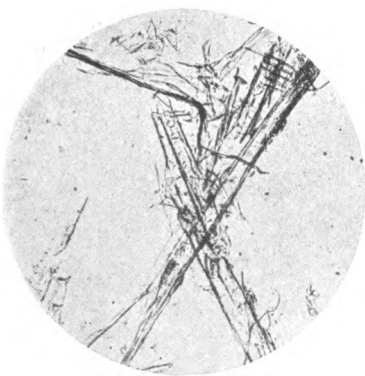
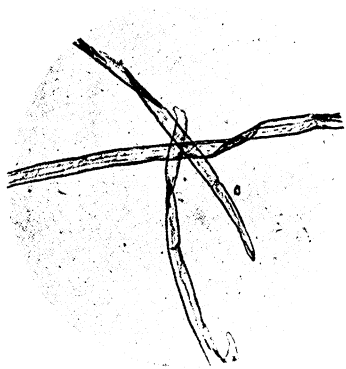


MECHANICAL WOOD PULP



SULPHITE WOOD PULP

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A TEXT-BOOK

OF

PAPER-MAKING

BY

C. F. CROSS AND E. J. BEVAN

THIRD EDITION

Containing Additional Matter, and in part Re-written, with collaboration of J. F. BRIGGS

London:
E. & F. N. SPON, LTD., 57 HAYMARKET

New York:
SPON & CHAMBERLAIN, 123 LIBERTY STREET

1907

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PREFACE

TO

THE THIRD EDITION

THE relatively rapid sale of the Second Edition is an indication of the growing interest in the Technology of Paper-making, and of approval of the general plan of this work.

Our treatment of the subject is designed to keep general principles to the forefront, and on this view the processes of the mill are treated as illustrations. We consider that a text-book cannot substitute the working experiences of the mill, and the more practical details of construction and manipulation can only be mastered as a matter of personal experience. To import these would only have the effect of overloading the matter and obscuring the scientific perspective.

Retaining the general plan and arrangement, the matter has been subjected to thorough revision ; many sections have been re-written with substantial additions.

We are especially indebted to Messrs. Longmans, Green and Co., Paternoster Row, London, for the privilege of reproducing portions of the text of the work on 'Cellulose' (CROSS AND BEVAN, 1895), of which they are Publishers, and have again to accord our acknowledgment to the various engineering firms for Contributions appearing in the text, with which they

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have favoured us. Messrs. BERTRAMS, Ltd., have, also, been kind enough to provide us with several drawings specially prepared.

The work of general revision has been in the hands of Mr. J. F. BRIGGS who has also contributed the matter of Chapter XII.

Mr. CLAYTON BEADLE has co-operated in various ways, and has specially contributed matter to the sections dealing with Beating—Paper Testing—Water-Supply—and Statistics. In the last named he was able to avail himself of the assistance of Mr. A. DYKES SPICER, whose valuable special work on the subject has recently issued from the press.

4 NEW COURT, LONDON:
1907.

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EXTRACT FROM THE PREFACE TO THE FIRST EDITION

OUR object in writing this book has been to bring before students and others the principles upon which scientific paper-making should be conducted, a concise exposition of which has not, we believe, been hitherto attempted.

Considerable prominence has been given to this aspect of the subject, possibly at the expense of what some may consider more essential details.

A belief in the importance of a thorough scientific training for paper-makers has dictated the style and purpose of the book.

We have not thought it necessary to enter into minute details respecting the construction of machinery, etc.; for these the reader is referred to such works as Hofmann's Treatise on the Manufacture of Paper.

Much of the scientific portion is here published for the first time. Part of it has already appeared in the form of papers read before various societies.

The chapter relating to the Treatment of Wood formed the subject of an essay, which obtained the prize offered by the Scottish Paper-makers' Association, in connection with the Edinburgh Forestry Exhibition, 1884.

4 NEW COURT, LONDON:
1888.

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EXTRACT FROM
THE PREFACE TO THE SECOND EDITION

In preparing this present Edition we have adhered strictly to the original plan and scope of the work, which is that of a text-book of principles, and not either an exhaustive treatise or a minutely descriptive manual of the manufacturing art. We have endeavoured at the same time to bring the matter of the book to the level of later developments, some of which are of such importance as to necessitate the re-writing of certain sections, notably those dealing with the Chemistry of Cellulose and the operations of Sizing, Loading and Colouring. Our aim is to present the subject to the reader according to its scientific perspective; to furnish a guide for the student or apprentice in acquiring his practical experience to the best advantage, and for those who have a working experience of Paper-making, in reviewing either for pleasure or profit, the multitude of facts to be observed in the daily routine of the mill.

4 New Court, London:
1900.

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PAPER-MAKING.

INTRODUCTORY.

PAPER-MAKING is essentially a mechanical art, consisting as it does in the production of a continuous web or fabric by aggregating together structural units of relatively minute dimensions.

These, the essential components of paper, are the vegetable fibres, first isolated from the fibrous raw materials by operations of both mechanical and chemical nature, and then further resolved or broken up by mechanical treatment.

But, though the actual paper-making processes are of the mechanical and physical order, they involve auxiliary chemical processes of fundamental importance. Moreover, there is a special chemistry of the fibrous components and of the auxiliary agents used in the making and finishing of papers, to know which is a necessary equipment of the paper-maker.

In presenting this brief outline of first principles, we cannot overrate the importance of a thorough grasp of the composition and constitution of the plant fibres, as the necessary foundation for the intelligent conduct of paper-making, and to this subject we will at once proceed.

Careful study of a mature flowering plant will show that it is made up of structural elements of two kinds, viz. fibres and cells, which to use a rough parallel, we may liken in function to the bricks and mortar of a house. It is the former which admit of the many extended uses with which we are

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familiar in the arts of spinning and weaving, and which constitute the fabrics which are the most indispensable to our civilised life. For the most part, as we know, fibres and cells are aggregated together into compound tissues, and a process of separation is therefore a necessary preliminary to the utilisation of the former. The cotton fibre is the only important exception to this general condition of distribution. Here we have the seed envelope or perisperm converted into a mass of fibres, and these, by a spontaneous process accompanying the ripening, so isolated as to be immediately available. Next in order, in point of simplicity of isolation, are those fibrous masses, or tissues, which, although components of complex structures, exhibit a greater cohesion of their constituent fibres than adhesion to the contiguous cellular tissues with which they go to build up the plant. Into such a tissue the 'bast,' or inner bark layer of shrubs and trees, more especially those of tropical and sub-tropical regions, frequently develops; and it is, in fact, this bast tissue, graduating in respect of cohesion of its constituent fibres, from a close network such as we have spoken of, to a collection of individual fibres or fibre-bundles disposed in parallel series, which supplies the greater part of the more valuable of the textile and paper-making fibres; we may instance flax, hemp and jute, each of which is the basis of an enormous industry. According to the degree of adhesion of the bast to the contiguous tissues, or, in another aspect, according to its lesser aggregate development, so is the difficulty of isolation and the necessity of using processes auxiliary to the mechanical separation of the tissue.

It is worthy of note here that the Japanese paper with which we are in these times so familiar, is prepared by the most primitive means from the bast of a mulberry (*Broussonetia papyrifera*); the isolated tissue, consisting of a close network of fibres, is simply cut and hammered to produce a surface of the requisite evenness, and the production of a web of paper is complete. In isolating the bast fibres employed in the textile industries, a preliminary partial disinte-

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gration of the plant stem is brought about by the process of steeping or retting, by which the separation of fibre from fleshy or cellular tissue is much facilitated.

Last in order of simplicity of distribution, we have the fibres known to the botanist as the fibro-vascular bundles of leaves and monocotyledonous stems, these bundles being irregularly distributed through the main cellular mass, and, consequently, by reason of adhesion thereto, much more difficult of isolation. For this and other reasons, more or less in correlation with natural function, we shall find this class of raw material lowest in value to the paper-maker.

It is necessary at this stage to point out that the work of the paper-maker and that of the textile manufacturer are complementary one to the other, and the supply of fibrous raw material is correspondingly divided: it may be said, indeed, that the paper industry subsists largely upon the rejecta of the textile manufactures. The working up of discontinuous fibre elements into thread, which is the purpose of the complicated operations of the spinner, is conditioned by the length and strength of these ultimate fibres. Paper-making, on the other hand, requires that the raw material shall be previously reduced to the condition of minute sub-division of the constituent fibres, and therefore can avail itself of fibrous raw material altogether valueless to the spinner, and of textile materials which from any cause have become of no value as such. To the raw materials of the paper-maker, which we have briefly outlined above, we must therefore add, as a supplementary class, textiles of all kinds, such as rags, rope, and thread.

During the latter part of this century, and in response to the enormously increased demands upon the sources of supply, there has come the exploitation of the fibrous woods for paper-making purposes.

Having thus acquired a general idea of the sources of our raw materials, we must study more closely the substances themselves; and, first of all, we must investigate them as we should any other chemical substance, i.e. we must get to

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understand the nature and properties of the matter of which the vegetable fibres are composed. While these exhibit certain variations, which are considerable, the substances present a sufficient chemical uniformity to warrant their being designated under a class name : this name is Cellulose. The prototype of the celluloses is the cotton fibre.

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CHAPTER I.

CELLULOSE.

CELLULOSE is the predominating constituent of plant tissues and may be shortly described as the structural basis of the vegetable world. Constituting, as it does, the material framework or skeleton of the plant, or plant cell, this more permanent function implies a corresponding resistance to the destructive agencies of the natural world: in other words, considered as a chemical individual, cellulose is extremely inert, or non-reactive. It is resistant to the hydrolysing action of alkalis and acids, to oxidants; and, as a 'saturated' carbon compound, has no tendency to combine directly with the halogen elements, e.g. chlorine and bromine. These main features of its negative chemical characteristics are mentioned thus early in explanation of the methods employed for its isolation in the laboratory. Cellulose never occurs in the plant in the free state, but always in admixture or combination with other groups: members of the fatty series ('fat and wax' constituents); the aromatic series (colouring matters, tannins); the pectic group of more or less oxidised, and therefore acid, derivatives of the carbohydrates. These latter yield to the attack of one or other of the reagents towards which cellulose is inert; and hence the following general method of removing these 'impurities' in the form of soluble derivatives, and of isolating the cellulose as the resistant residue: (*a*) the fibrous raw material is boiled with a dilute solution of sodium hydrate (1–2 p.ct. NaOH), and, after thorough washing, is (*b*) exposed in the moist state to an atmosphere of chlorine gas; (*c*) it is again treated with boiling alkaline solution. By such treatment of the majority

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of vegetable tissues, the 'non-cellulose' constituents are removed, and a residue of cellulose obtained. A slight treatment with a bleaching agent, to remove residues of coloured impurities, and a final washing with alcohol and ether, complete the purification, and the cellulose is obtained as a mass of 'ultimate fibres' of pure white colour, more or less translucent.

Though purified by the removal of 'non-cellulose' groups, such as above indicated, the residue of cellulose is not necessarily 'pure' in the sense understood by the chemist, that is, it cannot be taken to represent a single homogeneous substance.

On the contrary, we shall show that the paper-makers' 'celluloses'—obtained by a large variety of drastic treatments of fibrous raw materials—are mixtures of celluloses of different constitution.

Cotton cellulose, however, when fully purified, may be regarded as a chemically pure substance, and in setting forth the outline of the chemistry of cellulose, we shall at first confine ourselves to this typical representative of the group.

Empirical Composition.—Cellulose is a compound of carbon, hydrogen, and oxygen, united in the percentage proportions :—

C	44·2
H	6·3
O	49·5

corresponding with the statistical formula $C_6H_{10}O_5$, by which also it is defined as a 'carbohydrate.' The above numbers represent the composition of the 'ash-free' cellulose. All vegetable tissues contain inorganic or mineral constituents, of which a certain proportion is retained by the cellulose, isolated as described, or by any of the processes practised on the large scale in the arts. The celluloses burn with a quiet luminous flame, leaving these inorganic constituents as an ash. In bleached cotton the average proportion of ash is 0·1–0·4 p.ct.

In the preparation of filter paper for chemical use it is important to reduce this impurity to a minimum, which is effected by treatment with hydrofluoric and other acids. 'Swedish'

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filter paper contains 0·03–0·05 p.ct. ash constituents, representing about $\frac{1}{1000}$ mgr. per sq. cm. of area; and is the purest form of cellulose with which we can deal.

Cellulose and Water. Cellulose Hydrates.—All vegetable structures in the air-dry condition retain a certain proportion of water—or *hygroscopic moisture*, as it is termed—which is readily driven off on heating, but regained on exposure to the atmosphere under ordinary conditions. The mean percentage of this 'water of condition' varies from 6–12 in the several celluloses: in any given cellulose variations of 1–2 p.ct. from the mean number follow the variations in the hygrometric condition of the atmosphere. The factor of 'normal moisture' is of obvious importance in commercial dealings in celluloses. Thus, for the 'wood pulps' (celluloses), the 'standard moisture' commonly adopted is '10 p.ct.'—that is, 100 parts of the air-dry pulp yield on drying, at 100°, 90 parts dry cellulose. Conversely, in calculating from the basis of dry cellulose = a, to 'air-dry with 10 p.ct. moisture' = b, it is clear that $b = \frac{10}{9} a$. The proportion of water held by the celluloses in an atmosphere saturated with aqueous vapour is necessarily very much greater than in the ordinary atmosphere, partially saturated at the same temperature. The celluloses or compound celluloses (*supra*) as they occur in the plant are characterised by a wide range of hydration phenomena. Plant tissues in the early stages of growth take the form of gelatinous hydrates, the proportion of water combining with the organic colloid in these hydrates being very large, e.g. 80 p.ct. of the weight of the hydrate. The re-hydration of the mature celluloses to these forms is determined by certain reagents as a stage in their conversion into the fully soluble form. Such processes of solution of cellulose we proceed to consider.

Technical Applications.—By the wet-milling processes employed by the papermaker under the action of the Kollergang and the beating engine roll, the proportion of water entering into the cellulose fibres as the effect of hydration, can be increased almost to an unlimited extent. This effect is obtained

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purely by mechanical means, consisting of pressing, crushing, and rubbing the fibres in presence of water. By carrying this mechanical action to its limits, two industrial products are obtained (*a*) 'grease-proof' imitation parchment paper in which the original fibrous structure of the cellulose is still maintained in a considerable degree, and (*b*) 'cellulith' in which the mechanical hydration is carried to its fullest extent, being accompanied by the total breakdown of the fibrous structure, and the production of an amorphous cellulose jelly, which hardens on drying to a product of the consistence of bone, etc.

Solutions of Cellulose.—Cellulose is insoluble in water as in all simple solvents. In presence of certain metallic compounds, however, it combines with water, passing, as above described, through the conditions of gelatinous hydrates, and finally disappearing to form a homogeneous viscous solution.

This effect may be ascribed to the reciprocal interaction of acid and basic groups of the cellulose and the metallic compound—that is, to the formation of a species of colloidal double salt.

Of such solvents of cellulose the simplest is (1) ZINC CHLORIDE in concentrated aqueous solution (40 p.ct. $ZnCl_2$). The solution process requires the aid of heat (60–100°), and may be carried out as follows: 4–6 parts $ZnCl_2$ are dissolved in 6–10 parts water, and 1 part cellulose (bleached cotton) stirred in till evenly moistened. The mixture is digested at first at 60–80°, when the cellulose is gelatinised; the solution is completed by exposure to water-bath heat, stirring from time to time, and replacing the water which evaporates. In this way a homogeneous syrup is obtained. The solution is entirely decomposed by dilution, the cellulose being precipitated as a hydrate in combination with zinc oxide. On washing with hydrochloric acid a pure cellulose hydrate is obtained, the quantity recovered being approximately equal to the original cellulose taken. When precipitated by alcohol, a compound of cellulose and zinc oxide is obtained with 18–25 p.ct. ZnO, i.e. in the approximate molecular ratio $2\,C_6H_{10}O_5ZnO$.

Technical Applications.—(*a*) The precipitation of the syrupy

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solution by alcohol is of such a character as to permit of a continuous production of thread or film, the solution being 'squirted' under pressure from a fine glass orifice into the alcohol. The thread, when purified, is carbonised in close vessels, to form the very resistant carbon constituting the filament for incandescent electric lamps. (*b*) *Vulcanised fibre* is produced by treating a suitable paper (1 part) with a zinc chloride of 65–75° B (4 parts). When the constituent fibres are superficially gelatinised, the sheets are welded together under pressure into very compact masses. These are then purified, and subjected to further treatment to render them waterproof.*

(2) Zinc Chloride and Hydrochloric Acid.—If the $ZnCl_2$ is dissolved in twice its weight of aqueous hydrochloric acid (40 p.ct. HCl), a solution is obtained which dissolves cellulose rapidly in the cold. If quickly diluted the cellulose is recovered with but little change, but on standing it is resolved into products of lower molecular weight (dextrins, etc.) entirely soluble in water. The solution is a useful aid to investigations in the laboratory, and is also applied in the production of 'vulcanised fibre.'

(3) Ammoniacal Cupric Oxide. — The solutions of the cuprammonium compounds generally, in presence of excess of ammonia, attack the celluloses rapidly in the cold, forming a series of gelatinous hydrates, passing ultimately into fully soluble forms. The solutions of the pure cuprammonium hydroxide are more active in producing these effects than the solutions resulting from the decomposition of a copper salt with excess of ammonia. Two methods are in common use for the preparation of these solutions, which should contain—

10–15 p.ct. ammonia (NH_3).
2·0–2·5 p.ct. copper (as CuO).

(1) Hydrated cupric oxide is prepared by precipitating a solution of cupric sulphate at 2 p.ct. strength with a slight excess of sodium hydrate, also in very dilute solution. The

* German Patent 3181 (1878): C. Hofmann, Prakt. Handb. Papierf., p. 170.

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precipitate is washed till entirely free from alkali. The original solution in which the precipitation takes place, and the water used in washing, should contain a small portion of glycerin, 0·05 to 0·10 p.ct. The washed precipitate is fully drained, and then mixed with a quantity of a 10 p.ct. solution of glycerin—in contact with which it may be preserved unchanged in stoppered bottles. Prior to dissolving in 15–20 p.ct. NH_3 for use, the oxide may be washed free from glycerin, should the presence of the latter be objectionable.*

(2) Metallic copper in the form of sheet or turnings, or better still, as the fine powder used in decorative work ('Naturkupfer'), is placed in a cylinder and covered with strong ammonia; air is caused to bubble through the column of liquid at a rate calculated to forty times the volume of the liquid used per hour. In about six hours a liquid of the requisite composition is obtained.

Solutions of cellulose of 5–10 p.ct. (cellulose) strength, are readily prepared by digestion in the cold with 10–20 times its weight of the solution. The solutions are rather 'ropy' and gelatinous than viscous. The cellulose is readily precipitated from the solutions: (*a*) by neutral dehydrating agents, such as alcohol, sodium chloride, and other salts of the alkalis; (*b*) by acids. In the latter case the cellulose is precipitated in the 'pure' state, i.e. free from cupric oxide. It retains a large proportion of water of hydration. On drying by heat, the gelatinous hydrate changes by molecular aggregation into compact horny masses.

Technical Applications.—This property of gelatinising and dissolving cellulose has been taken advantage of in important industrial applications of the cuprammonium compounds. Vegetable textile fabrics and paper, passed through a bath of the cuprammonium hydroxide, are 'surfaced' by the film of gelatinised cellulose, which retains the copper oxide (hydrate) in such a way that it dries to a bright malachite green colour, the ammonia of course escaping. By this treatment the fibres are further compacted together, and the fabric acquires a

* Fassbender: Berl. Ber. **13**, 1822.

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water-resistant character; the presence of the copper oxide is also preservative against the attacks of mildew, insects, etc. If the fabrics are rolled or pressed together when in the gelatinised condition, they become welded together on drying, and a variety of compound textures are produced in this way. The fabrics are sold in this country under the style of 'Willesden' goods. Recently, also, the solution has been applied to the production of an artificial thread of high lustre, a so-called 'artificial silk,' or lustra cellulose. The preparation of structureless solutions for this application is much facilitated by previous treatment of the cellulose by the 'mercerising' process (p. 18). The solution is projected through fine orifices (0·10–0·15 mm.) into a bath of sulphuric acid or caustic soda; the precipitated cellulose hydrate, in the form of thread, is wound off in continuous length; a number of these unit threads are brought together and suitably twisted (150–300 per metre) to form textile thread.

Cellulose and Hydrolytic Agents.—We have called attention to a common feature of the action of the various aqueous solvents of cellulose, that is, a simultaneous attack upon OH groups of the cellulose of opposite function. This amphoteric function or character of cellulose is more clearly brought to demonstration by the reactions about to be described. We may assume that cellulose yields to the action of zinc chloride by reciprocal interaction of its OH groups with those of the salt in solution, and that the dissolution of the cellulose is therefore due to a species of double salt formation.

An incipient activity of this kind is manifested by cellulose in contact with highly dilute solutions of alkalis and acids, the active reagent being absorbed by the cellulose in perceptible degree. The amount, though small, is definite, and sufficient to allow of the establishment of a definite *ratio* of absorption from equivalent solutions of alkalis and acids. Thus, with typical members of the two groups, the molecular ratio of absorption is 10 NaOH : 3 HCl.* The phenomenon has been more recently studied from the independent stand-

* Mills.

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point of thermal equilibrium. It has been shown that when pure cotton is plunged into dilute solutions of the acids and alkalis, liberation of heat takes place. The rise of temperature was found to be slow, and, under the conditions chosen for the experiments, ceases after the lapse of seven to eight minutes.

The following are typical results in calories per 100 grms. of cotton :—

—	KOH.	NaOH.	HCl.	H_2SO_4.
Raw cotton . .	1·30	1·08	0·65	0·60
Bleached . . .	2·27	2·20	0·65	0·58

L. Vignon.

It would appear from these results that cellulose has the properties of a feeble acid, and of a yet feebler base. From the comparative insignificance of the 'affinities' involved, it might be inferred that they may be neglected in practical and industrial operations. So far from this being the case, it must be remembered that the combination of cellulose with colouring matters, i.e. the dyeing properties of the fibre substance, are largely dependent upon a play of affinities of this particular order. So also the auxiliary processes of mordanting, in which the fibre absorbs both acidic and basic oxides from dilute saline solutions ; these oxides, in combination with the fibre substance, enable it in turn to take up particular colouring matters from their solutions. Formerly it was much discussed as to whether dyeing phenomena were of the 'physical' or 'chemical' order.* The modern view does not concern itself so much with definitions as to insist that the phenomena are molecular. This chemical aspect is prominent in the reciprocal play of acid and basic functions of the constituent groups of both fibre-substance and colouring matter (and mordant) ; the 'physical' side is brought into

* Cellulose Researches, Cross and Bevan, 1906.

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evidence by certain properties of the fibres which are bound up with their minute structure, and which evidently play an important part in the absorption of reagents from solution, viz. the phenomena of *capillary transmission* of liquids. Schönbein appears to have been the first to observe that strips of unsized paper, of which one end is placed in an aqueous solution, e.g. of a metallic salt, will absorb and transmit the water more rapidly than the dissolved salt, which is therefore 'filtered out'; further, that to the various salts cellulose manifests varying degrees of resistance to transmission in solution. These phenomena have been further studied by Lloyd,* for metallic salts, more recently by E. Fischer and Schmidmer,† and by F. Goppelsroeder for various colouring matters;‡ the results of their observations constituting the beginnings of a method of capillary analysis or separation. Without further discussing the phenomena from a theoretical standpoint, we may point out that they are of direct practical moment to the paper-maker: since, first, they have to be reckoned with in every one of his manufacturing operations; secondly, in one of the most important applications of paper, viz. for writing purposes, the penetration of the paper by the ink, its indelible fixation, and the kind of press copy obtainable, are points largely affected or determined by such inter-actions as we have been considering.

It will be remembered that we have followed up the various matters dealt with in this section from the initial observation of the behaviour of cellulose to typical hydrolytic agents in cold dilute solution. These are absorbed, as we have seen, to form what we may term contact compounds, and they are an index of the hydrolytic changes which are determined by these compounds acting in more concentrated forms and at higher temperatures. *Hydrolysis* is essentially a process of resolution or decomposition: it is the loosening or undoing of a bond of union through combination with the elements of water. The agent which determines the change

* Chem. News, **51**, 81. † Liebig, Ann., **272**, 156.
‡ Berl. Ber., **20**, 604.

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is the hydrolytic agent: and of such agents the most important are the (*a*) acids and (*b*) alkalis on the one hand, and (*c*) on the other, a class of carbon compounds known as soluble or unorganised ferments, or by the more modern term Enzymes. Cellulose yields to hydrolysis of both types.

(*a*) ACIDS.—The mineral acids of concentration equal to semi-normal at the boiling temperature, rapidly disintegrate the fibrous celluloses, as a consequence of molecular changes in the fibre-substance. The modified cellulose is brittle and pulverulent. Its composition is changed to that of a *hydrate* of the formula $2.C_6H_{10}O_5 . H_2O$, and it is therefore termed hydro- or hydra-cellulose, the chemical properties of which are described in a later section. The time required for completing this change varies with the temperature and concentration of the acid. The acid treatments of cellulose textiles which are necessary incidents of bleaching and dyeing operations are carried out well within the limits of safety—for the most part in the cold ($<20°$ C.) and with acids of less than 2 p.ct. strength (HCl, H_2SO_4). In dyeing operations requiring an acid bath and the boiling temperature, 'free' mineral acids are as much as possible avoided, acetic acid being substituted—an acid of low hydrolysing activity, and without sensible action on cotton. Paper is usually finished from the machine with a slightly acid *reaction*, but the utmost care is required to insure the absence of 'free' acid.

(*b*) ALKALIS.—To alkaline solutions of equivalent strength, e.g. solutions of caustic soda of 1–2 p.ct. Na_2O, cotton cellulose is extremely resistant, even at temperatures exceeding 100°. The principal operations in the process of bleaching cotton and linen textiles are drastic alkaline treatments of this kind, whereby the non-cellulose constituents of the fibres are hydrolysed to products soluble in the alkaline lye. The oxidation processes which follow, e.g. treatment with the hypochlorites, permanganates, etc., in dilute solutions, although they may be regarded as the bleaching processes proper, really accomplish very little beyond removing residues or by-products of the alkaline treatment. It is also evident that resistance to

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alkaline treatment such as soaping, is a very important condition of the everyday uses of cellulose textiles.

At higher concentration and temperature the typical cellulose is attacked by the alkaline hydrates and converted into soluble derivatives. Thus, purified cotton cellulose digested three times in succession with solutions of 3 p.ct. Na_2O, was found to lose* :—

at 1 atm.	pressure	12·1 p.ct.
5	„	15·4 „
10	„	20·3 „

With solutions of 8 p.ct. Na_2O under similar conditions the losses were 22·0, 28·0 and 59·0 p.ct. The processes of isolating paper-makers' celluloses largely consist of severe alkaline treatments, the conditions of which require adjustment to secure the most complete removal of the non-cellulose constituents of the raw materials, with the minimum of action (hydrolysis) on the cellulose.

A process of estimating cellulose in fibrous raw materials in the laboratory, based upon the action of alkaline hydrates at elevated temperatures (150–180°), has been proposed by Lange.† The process rests upon the assumption that the celluloses are not attacked under the severe conditions of alkaline treatment adopted. This assumption cannot be maintained in view of the results above cited; the process has, moreover, been subjected to a careful critical investigation by Tollens,‡ who finds that it is subject to large and variable errors.

(*c*) ENZYMES.—A typical case of enzyme action is that of the conversion of the starches of cereals into fermentable sugars, in the operations (1) of malting the grain, (2) of 'mashing' the malt with water, to the solution or wort in which the sugars formed from the starch are in a condition to yield readily to the attack of the yeast-cell, undergoing further hydrolysis under the action of the yeast enzyme, and being

* H. Tauss, Journ. Soc. Chem. Ind. 1889, 913; 1890, 883.
† Ztschr. Physiol. Chem., **14**.
‡ Suringar and Tollens, Ztschr. Angew. Chem. 1896, No. 23.

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finally broken down to alcohol and carbonic acid. The starches resemble the typical celluloses in the following particulars: they have the same empirical formula $n[C_6H_{10}O_5]$; they are poly-anhydrides of hexose molecules, each hexose molecule losing water in the proportion of one molecule—thus $m.2C_6H_{12}O_6 - m.2H_2O$—in *condensing* to form the anhydride; the highly complex molecule of the latter takes up water under the influence of hydrolytic treatments—in successive stages, *but special to each*—giving a similarly complex series of intermediate (i.e. partially hydrated) molecules, these breaking up finally (i.e. by complete hydration) to the typical hexose, dextrose.

Starch, under the influence of the enzyme of malt, termed *diastase*, yields the series of dextrins, amylins, malto-dextrins, maltose, and finally dextrose. To convey some idea of the complications presented by the series, it may be noted that it is necessary to expand the original starch molecule to $5[C_{12}H_{20}O_{10}]_{20}$. The first effect of hydrolysis is to split this into a resistant *dextrin* of the formula $[C_{12}H_{20}O_{10}]_{20}$, and a group of amylins representing the remaining four-fifths of the molecule which pass through further hydration stages represented by such formulæ as $[C_{12}H_{20}O_{10}]n + H_2O$, maltose groups being successively formed and split off. Yeast, again, secretes an enzyme termed *invertase*, which hydrates the crystallisable but still complex sugars such as maltose and cane sugar [both $C_{12}H_{22}O_{11}$] to the simple hexose $C_6H_{12}O_6$.

No enzyme has yet been discovered which enables us to carry out a similar 'conversion' or hydration of cellulose in the laboratory. That such actions take place in plant life has been abundantly established. (*a*) In the germination of seeds the cell-walls (cellulose) are broken down to supply nutriment to the embryo. (*b*) In the attack of parasitic plants, dense structures of the 'host' are penetrated by the most delicate hyphæ of the invading organism by a dissolution and resolution of the original cellulose structure. (*c*) Brown and Morris have succeeded in cultivating the excised embryos of the cereals on artificial endosperms, and in showing that a cytohydrolytic

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enzyme is secreted which is sufficiently powerful in its action as to attack (i.e. hydrolyse) the typical cotton cellulose.

There are also certain characteristic destructive 'fermentations' of cellulose determined by specific organisms (soil bacteria), the products of which are the lower fatty acids and gaseous products, notably hydrogen and methane (Omeliansky). It has been stated recently, however, that whereas cotton, linen, and similar celluloses are readily fermented by these bacteria, the cellulose of wood (sulphite pulp) resists their attack. These resolutions must be preceded or attended by profound hydrolytic resolutions, but hitherto no intermediate products have been observed, such as might be expected to be produced by enzyme action. While, therefore, we have only an expectation to be furnished with the means of studying an enzyme hydrolysis, or dissection of cellulose, we are at present limited to the action of powerful reagents such as the concentrated mineral acids, which, in a later section, we shall show to resolve cellulose through a series of hydration products (amyloid, dextrins, dextrose) presenting many analogies with the starch-dextrose series above described.

Cellulose, therefore, while an analogue of starch, is differentiated from it by an enormously greater resistance to hydrolytic actions of all kinds, which must express a corresponding difference in constitution.

We have now to study the actions of hydrolytic agents in *their more concentrated forms*.

(a) **Alkalis.**—Cold solutions of the alkaline hydrates of a certain concentration exert a remarkable effect upon the celluloses. Solutions of sodium hydrate, at strengths exceeding 10 p.ct. Na_2O, when brought into contact with the cotton fibre at the ordinary temperature, instantly change its structural features, i.e. from a flattened riband with a large central canal is produced a thickened cylinder with the canal more or less obliterated. These effects in the mass, e.g. in cotton cloth, are seen in a considerable shrinkage of length and width, with corresponding thickening, the fabric becoming translucent at the same time. The results are due to a definite reaction

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between the cellulose and the alkaline hydrates, in the molecular ratio $C_{12}H_{20}O_{10}$: 2NaOH, accompanied by combination with water (hydration). The compound of the cellulose and alkali which is formed is decomposed on washing with water, the alkali being recovered unchanged, the cellulose reappearing in a modified form, viz. as the hydrate ($C_{12}H_{20}O_{10}.H_2O$). By treatment with alcohol, on the other hand, one half of the alkali is removed in solution, the reacting groups remaining associated in the ratio $C_{12}H_{20}O_{10}$: NaOH. The reaction is known as that of mercerisation, after the name of Mercer, by whom it was discovered and exhaustively investigated.

A more recent investigation of Pope and Hübner * should be studied by those who have a special interest.

Technical Applications.—Until quite recently, the observations of Mercer remained undeveloped. They are now applied on a large and increasing scale to the production of a silky lustre in cotton textiles. It is found that if during the action of the alkaline lye the cotton goods are kept under strain, the physical changes determined in the fibres enable it to produce that concentrated reflection of incident light which causes lustre.† These structural changes are permanent, persisting after the removal of the alkali by washing.

ALKALI CELLULOSE.—The compounds resulting from the union of cellulose and the alkaline hydrates, though of little stability—as we have seen—are still well-defined products. This fact is emphasised by the production from the alkali cellulose of two series of characteristic derivatives of cellulose: (*a*) the sulpho-carbonates; (*b*) the benzoates—which are described in later sections.

(β) The **Acids** in concentrated form act in two opposite directions upon cellulose: (1) they attack and resolve the cellulose complex by processes of condensation and hydrolysis; (2) they *combine* with the cellulose (OH groups) to form acid ethers or *esters*. These effects are not sharply separated, but form graduated or continuous series; those of the first group are no doubt determined by combination of the more basic OH groups

* J. Soc. Chem. Ind., **23**, 404. † Rev. Gen. d. Mat. Col. 1898.

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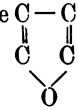
of the cellulose with the acid radicals, but these combinations are transitional in presence of water. We shall first describe the changes of this order determined by aqueous mineral acids.

HYDROCHLORIC ACID in presence of water rapidly converts the fibrous cotton cellulose into a friable substance, the formation of which is not attended by any visible changes; but, on subjecting the product to pressure or mechanical action, it becomes a more or less structureless powder.

This product, known as hydro- or hydra-cellulose, was first investigated as a cellulose derivative by A. Girard,* who regarded the product as a hydrate of empirical composition, $C_{12}N_{22}O_{11}$. The later researches of A. L. Stern† show, however, that products of this kind may be obtained without sensible change in composition; their formation is accompanied by the production of monoses (Girard), the cellulose undergoing a loss of weight. But the profound changes which are evidenced by destruction of the fibre, are those of the aggregate, which is entirely altered in constitution.

These reactions and compounds are of particular interest to the paper-maker, as he has to take special precautions to eliminate all possible conditions which might lead to their production. The special treatises on the subject should therefore be consulted. (See also 'Researches in Cellulose,' ii., p. 139).

Hydrobromic and hydriodic acids also produce similar destructive actions. Hydrobromic acid in presence of anhydrous ether effects a total resolution of the cellulose complex, and the end-product is brom-methyl furfural. The formation of this compound represents a complete removal of the OH groups of the cellulose, a resolution into unit groups of C_6 dimensions, and the further 'condensation' of these to the  ring of furfural.

SULPHURIC ACID.—Hydro-cellulose results also from the action, at ordinary temperatures, of sulphuric acid at certain

* Mémoire sur l'Hydrocelluloses. Paris, 1881. Gauthier-Villers.
† J. Chem. Soc., **85**. 336.

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dilutions. The following points have been established by C. Koechlin.* What may be called the critical concentration of the acid in regard to the production of hydro-cellulose lies between the limits 60–80° B. Thus, with the mixture of 3 vols. of the concentrated acid and 8 vols. water—i.e. an acid of 69° B. —at the ordinary temperature, its action upon cotton does not become evident till after three hours' exposure. With an aqueous acid containing 100 grams H_2SO_4 per litre and at 80° C., the first appearances of change in the cotton are noted at the expiration of five minutes; after thirty minutes' exposure there is sensible disintegration; after sixty minutes the conversion is complete, i.e. into a friable mass of hydro-cellulose.

The subjoined are analyses of specimens produced under very variable conditions of treatment of the cotton :—

—	(1)	(2)	(3)	(4)	$C_{12}H_{22}O_{11}$
Carbon . . .	42·10	42·50	42·04	41·80	42·1
Hydrogen . .	6·30	6·50	6·70	6·70	6·4
Oxygen . .	51·60	51·00	51·26	51·50	51·5

Viz. (1) and (2) by the action of sulphuric acid of 45° B.; (3) by the action of gaseous hydrochloric acid in presence of moisture; (4) by the action of dilute sulphuric acid (3 p.ct. H_2SO_4) at 60° C. The action of such acids, therefore, which do not combine with the cellulose to form definite *esters* (*infra*) is one of hydration and hydrolysis, the insoluble product tending to a limit represented by the formula $n[C_{12}H_{20}O_{10}.H_2O]$. The hydration of cellulose to such a product is attended by a gain of weight. But the reaction studied in the mass, i.e. as an aggregate effect, is always attended by *loss* of weight, the hydro-cellulose weighing less, and under some conditions of action of acids, much less than the original cellulose. This is due to a further hydrolysis of a portion of the cellulose to products soluble in water—tending, in fact, to the limit of extreme

* Bull. Mulhouse, 1888.

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hydrolysis to dextrose. The reaction, in fact, is a complicated one, condensation or dehydration playing an important part in the changes which may, in the net or aggregate effect, result in a hydration of the cellulose.

The properties of the hydro-cellulose are in some respects those of cellulose: it dissolves, though more readily, in the special solvents of cellulose; and combines, but also more readily, with nitric acid (*infra*) to form a similar series of nitrates. Generally, it is in all respects much more reactive.

It rapidly oxidises when heated at 100°, with discoloration; the brown-coloured products of oxidation are soluble in water, and reduce Fehling's solution. Hydro-cellulose is attacked by dilute alkalis and dissolved more or less; the solutions are yellow in colour and reduce Fehling's solution.

It is clear, therefore, that the main characteristics of the hydro-cellulose series is a progressive *hydrolysis* of the cellulose, with liberation of the CO groups of the constituent hexose units. These hydrolytic changes are attended by progressive structural disintegration, and the products have lost the characteristics of chemical inactivity. In all properties, therefore, which determine the industrial value of cellulose, and notably to the paper-maker, the hydro-celluloses are inferior, or degradation products.

Technical Applications.—The removal of vegetable fibres from mixed woollen refuse (shoddy), and of vegetable impurities from raw wool, is effected by acid treatments of various degrees such as we have described, to which the wool is resistant. To the paper-maker hydro-cellulose has first the negative importance that he has by all means to avoid its production in the finished web or sheet.

Sulphuric Acid. — Di- and tri-hydrate—$H_2SO_4 . 2H_2O$, $H_2SO_4 . 3H_2O$—produce a special series of hydration effects. Unsized paper plunged into sulphuric acid diluted previously with $\frac{1}{3}$ to $\frac{1}{4}$ its volume of water and cooled, is rapidly attacked, the paper becoming transparent, owing to the swelling and gelatinisation of the fibres. The reaction quickly becomes one of solution; but if the paper be transferred, after short

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exposure, to water, the acid compound is decomposed, and the resulting gelatinous hydrate is precipitated *in situ*. The product, after exhaustive washing and drying, is obtained as *parchment paper*. This modification gives a tough translucent sheet.

The hydrated compound itself, produced as described, from its resemblance to starch, has been termed *amyloid*. Its empirical composition is that of the hydro-celluloses, viz. $n\ [C_{12}H_{22}O_{11}]$, to which compounds also it is closely allied in chemical properties.*

Technical Application.—The process as described above is carried out industrially on 'continuous' machinery, the parchment paper being produced in endless length. The product is variously applied as a substitute for paper where resistance to water is required, as, for instance, in dialysing processes, where the parchment paper is used as the separating but permeable membrane. Another characteristic feature of the product is that it is, more or less, oil or grease-proof.

NITRIC ACID of sp. gr. 1·4 also produces (without oxidation) an effect of a similar character. A short immersion of unsized paper, e.g. filter paper, in the acid, followed by copious washing, has a considerable toughening action, attended by a shrinkage in linear dimensions of about $\frac{1}{10}$.† The effect is made use of in the laboratory as a convenient method of toughening filter papers when required to stand exceptional fluid pressures.

To follow a strictly logical order of treatment, we should describe here the compounds of cellulose formed by direct union with acid radicals, viz. the cellulose esters, such as the nitrates, sulphates, and acetates, which are formed on bringing cellulose in contact with the respective concentrated acids or anhydrides. But we defer the mention of these to a later section, as they have only an indirect bearing on the technology

* See 'Soluble and Insoluble Colloidal Cellulose and Composition of Parchment Paper.' Guignet. Compt. Rend., **108**, 1258.

† See Journ. Chem. Soc., **47**, 183. (See also Knecht. Berl. Ber., 1904, 549, and 'Researches on Cellulose,' **2**, p. 48).

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of paper-making; and we have to continue the discussion of the more important relationships of cellulose to water, of which we have a conspicuous illustration in a highly characteristic group of water-soluble derivatives, which are, in effect, esters: these are the sulpho-carbonates of cellulose, or salts of cellulose-xanthic, or xanthogenic acid.

Sulpho-Carbonates of Cellulose [Cellulose xanthogenic acid].—We have shown that cellulose combines with the alkaline hydrates, and when the resulting compound, or alkali-cellulose (hydrate), is exposed to the action of carbon disulphide at the ordinary temperature, a simple synthesis takes place, which may be formulated by the typical equation:

$$X.OH + NaOH + CS_2 = CS\begin{matrix}OX\\SNa\end{matrix} + H_2O$$

The best conditions for the reaction appear to be when the reagents are brought together in the molecular proportions:

$$\begin{matrix}C_6H_{10}O_5\\162\end{matrix} \quad \begin{matrix}2NaOH\\2\times 40\end{matrix} \quad \begin{matrix}CS_2\\76\end{matrix} \quad [30\text{–}40H_2O];$$

the second NaOH group being in associated union with the cellulose complex, which reacts, therefore, as an alkali cellulose. The resulting compound may therefore be described as an alkali-cellulose-xanthate. It is perfectly soluble in water, to a solution of extraordinary viscosity. The course of the reaction by which it is produced is marked by the further swelling of the mercerised fibre and a gradual conversion into a gelatinous transparent mass, which dissolves to a homogeneous solution on treatment with water.

To carry out the reaction in practice, bleached cotton or wood-pulp is treated with excess of a 15–18 p.ct. solution of NaOH, and squeezed till it retains from 2·5–3 times its weight of the solution. It is then placed in a closed vessel with carbon disulphide, the quantity being about 50 p.ct. of the weight of the cellulose. After standing about three hours at

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ordinary temperatures, water is added sufficient to cover the mass, and the further hydration of the compound allowed to proceed spontaneously some hours (e.g. over night). On stirring, a homogeneous liquid is obtained, which may be diluted to any required degree.

Thus prepared, the crude solution is of a yellow colour, due to by-products of the reaction (trithiocarbonates). The pure compound is obtained either by treatment of the solution with saturated brine or with alcohol. It forms a greenish-white flocculent mass or coagulum, which redissolves in water to a colourless or faintly yellow coloured solution. Solutions of the salts of the heavy metals added to this solution precipitate the corresponding xanthates. Iodine acts according to the typical equation :

$$CS\begin{matrix}OX\\SNa\end{matrix} + \begin{matrix}XO\\NaS\end{matrix}CS + I_2 = 2\,NaI + CS\,.\begin{matrix}OX\\S\text{—}S\end{matrix}\cdot\begin{matrix}XO\\\end{matrix}CS$$

The compound, which may be described as a cellulose dioxythiocarbonate, is precipitated in the flocculent form ; it is redissolved by alkaline solutions in presence of reducing agents, to form the original compound.

The most characteristic property of the cellulose xanthates is (*a*) their *spontaneous decomposition* into cellulose (hydrate), alkali, and carbon disulphide—or products of interaction of the latter. When this decomposition proceeds in aqueous solution, at any degree of concentration exceeding 1 p.ct. cellulose, a jelly or coagulum is produced, of the volume of the containing vessel. These highly hydrated modifications of cellulose lose water very gradually, the shrinkage of the 'solid' taking place symmetrically. The following observations upon a 5 p.ct. solution (cellulose), kept at the ordinary atmospheric temperature, will convey a general idea of the phenomena attending the regeneration of cellulose from the alkali xanthate. The observations were made upon the solution kept in a stoppered cylinder ; after coagulation, the solution, expressed from the coagulum of cellulose by spontaneous shrinkage, was removed at intervals. Original volume of solution, 100 c.c.

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	Time in Days.	Vol. of cellulose hydrate.	Diff. from 100 c.c. = vol. expressed.
Coagulation	8th day		
First appearance of liquid	11th ,,	c.c.	c.c.
	16th ,,	98·0	2·0
	20th ,,	83·5	16·5
	25th ,,	72·0	28·0
	30th ,,	58·0	42·0
	40th ,,	42·8	57·2
	47th ,,	38·5	61·5

The shrinkage from a 5 p.ct. to a 10 p.ct. coagulum of cellulose hydrate is therefore extremely slow and fairly regular; from 10–12 p.ct. there is considerable retardation; and at 12–15 p.ct. the coagulum may be considered as a hydrate, stable in a moist atmosphere. It follows from these observations that if a 10–12 p.ct. solution be allowed to coagulate spontaneously, the resulting cellulose hydrate will undergo very small shrinkage if kept in a moist atmosphere. These observations indicate the uses which can be made of the solution in preparing cellulose casts and moulds.

As regards the problem of hydration and dehydration of the cellulose there are, of course, other methods of approximately determining the 'force' by which the water molecules are held. It is a problem of wide significance, by reason of the important part played by such hydrates in the economy of plant life. Further investigations of the problem, therefore, by the various known methods are being prosecuted.

(*b*) *Coagulation by Heat.*—The solution may be evaporated at low temperatures to a dry solid, perfectly re-soluble in water. If heated at 70–80°, however, the solution thickens; and at 80–90° the coagulation (i.e. decomposition) is rapidly completed. If the solution be dried down at this temperature in thin films, it adheres with great tenacity to the surface upon which it is dried. On treatment with water, however, the cellulose film may be detached, and when freed from the by-products of the reaction the cellulose is obtained as a homogeneous transparent colourless sheet or film, of great toughness, which, on drying, hardens somewhat, increasing in toughness and preserving a considerable degree of elasticity. From the

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properties of the solution and of the cellulose regenerated from it, it will be seen that both are capable of extensive applications.

QUANTITATIVE REGENERATION OF CELLULOSE FROM SOLUTION AS THIOCARBONATE. — Very careful experiments have been made to determine the proportion of cellulose recovered from solution as thiocarbonate. Weighed quantities of Swedish filter paper were dissolved by the process, and the solutions treated as follows: (*a*) allowed to 'solidify' spontaneously at 15–18°; (*b*) coagulated more rapidly at 55–65°; (*c*) sulphurous acid was added in quantity sufficient to combine with one-third of the alkali present in the solution—the resulting solution being colourless: this was then set aside to coagulate spontaneously. The regenerated celluloses were exhaustively purified, by boiling in sodium sulphite solution, digesting in acid, digesting in water, etc., and, repeating the treatments until pure, they were finally dried at 60° and finished at 100°.

The following results were obtained :—

	Weight of original cellulose.	Weight of regenerated cellulose.
(*a*)	1·7335	1·7480
(*b*)	1·7415	1·7560
(*c*)	1·8030	1·8350

The results show a net difference of 1·1 p.ct. (increase), a quantity which, for practical purposes, may be neglected. As, however, the empirical composition of the regenerated cellulose indicates hydration to $4C_6H_{10}O_5.H_2O$ (*infra*), and a corresponding gain of 2·7 p.ct., it appears that there is a slight hydrolysis of even this very pure form of cellulose to soluble products. From subsequent observations (p. 41) it will appear that the hydrolysis falls upon an oxycellulose, probably present in all bleached celluloses.

The *cellulose regenerated* from the thiocarbonate differs from the original cellulose, so far as has been ascertained, in the following respects :—

(1) Its *hygroscopic moisture*, or water of condition, is some 3–4 p.ct. higher, viz. from 9–10·5 p.ct.

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(2) *Empirical Composition.*—The mean results of analysis show C = 43·3, H = 6·4 p.ct., which are expressed by the empirical formula, $4\,C_6H_{10}O_5 . H_2O$.

(3) *General properties*, in the main are identical with those of the original, but the OH groups of this cellulose are in a more reactive condition, in relation to bases, but less reactive towards acid groups; notably towards esterifying reagents, under acid conditions of reaction.

As regards reaction in aqueous solution, we may notice that it has a superior dyeing capacity, and also combines with the soluble bases to a greater extent: e.g. if left some time in contact with a normal solution of sodium hydrate, it absorbs from 4·5–5·5 p.ct. of its weight of NaOH in combination.

Towards the special solvents previously described it behaves similarly to the normal or fibrous cellulose; the solutions obtained are, however, more viscous and less gelatinous.

The thiocarbonate reaction throws light on that somewhat vague quantity, the 'reacting unit' of cellulose. We use this term in preference to that of molecular weight; for the latter quantity can be determined only for bodies which readily assume the simplest of states, and which can be ascertained by physical measurements to be in that state; whereas in the case of cellulose the ordinary criteria of molecular simplicity are quite inapplicable.

Quantitative Methods Applicable to the Analysis of Viscose Solutions.—(1) Cellulose xanthic acid is an acid of greater 'strength' than the organic monocarboxylic acids, and its salts are not decomposed by acetic acid. This is of considerable importance in the analysis of solutions of these products, as the by-products accompanying them are salts of the carbonic and sulphocarbonic series and entirely decomposed by acetic acid. Whereas, a 'mineral' acid necessarily attacks the whole of the alkali present in a crude viscose, acetic acid attacks only the by-products converting the alkali into acetate; the alkali combined with the CSS-group resists its action. A differential acidimetric titration therefore measures the latter or 'xanthate soda.'

(2) Similarly after acidification with acetic acid, the char-

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acteristic xanthate remaining unaffected, it may then be brought into reaction with a standard iodine solution. In a titration with iodine we have to take into account the quantity absorbed in oxidising the decomposed by-products. The latter quantity is estimated in a parallel experiment under identical conditions, except that sulphuric acid is added in excess.

(3) *Cellulose* is estimated by weighing a portion of the viscose, spreading on a glass plate, drying down and fixing the cellulose, which is obtained as a transparent film.

(4) *Total alkali* is estimated by any of the usual processes. The by-products may be estimated in terms of sulpho-carbonates, sulphides, and polysulphides by the standard methods.

Analyses of viscose have shown that, whereas the proportions of the original reacting groups are :—

$$C_6H_{10}O_5 \; ; \; 2NaOH \; ; \; CS_2,$$

and represent the minimum quantities of the reagents brought into contact with the cellulose to determine a full conversion of the latter into a water-soluble product, the xanthate obtained is subject to a progressive decomposition or dissociation, and in the solution passes through the following stages :—

(*a*) $C_{12}H_{19}O_9$ O CSS Na—characteristic of viscose twelve to twenty-four hours after preparation ; this passes continuously, without any visible break into

(*b*) $C_{24}H_{39}O_{19}$ O CSS.Na, which is insoluble in weak saline solutions, and therefore represents the condition of the xanthate in the mass of viscose, which has coagulated and set spontaneously. Xanthates more advanced in the dissociation series, are insoluble even in pure water, but soluble in solutions of the alkaline hydrates. In addition, therefore, to the acidity due to the configuration XO. CSS, there are OH groups of the cellulose itself, of sufficiently pronounced acid function to combine with an alkaline group to such an extent that the physical properties of the aggregate are modified.

In discussing this reaction we have left out of consideration the part played by the water. It may be noted that a 1 p.ct. solution of cellulose (as thiocarbonate) will 'set' to a firm jelly

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of hydrate, of the volume of the containing vessel ; and that even at 0·25 p.ct. cellulose, gelatinisation of the liquid occurs in decomposition. We have also pointed out that a hydrate containing only 10 p.ct. cellulose, is a substantial solid which gives up water with extreme slowness.

Cellulose, therefore, affords conspicuous illustrations of the property which the 'colloids' have, as a class, of 'fixing' water, and of the modes in which this property takes effect. In regard to the causes underlying this peculiar relationship to water, we know as yet but little. It is to be noted that the group of colloids comprises bodies of very various chemical function, acids, bases, salts and compounds of mixed function, as in the complex carbohydrates and proteids.

The common property of the group is that of continuous combination with water to indefinite limits (hydrosol state) and the reversal of the process to the state of a solidified jelly or 'hydrogel.' It is now generally recognised that these phenomena are related to a highly complex interior dissociation of these compounds, which are of more or less pronounced amphoteric function. A general theory of the colloidal state is in course of active evolution. It is not sufficiently matured to warrant any final conclusions or statements. Students who wish to prosecute the subject are referred more particularly to the following publications,* and are reminded that cellulose, as the prototype of the carbohydrate colloids is marked out as the most fruitful arena of investigation.

Technical Applications.—The solutions of cellulose in the form of sulphocarbonate are prepared for industrial use at concentrations of 10–20 p.ct. (cellulose) according to requirement. The product in this form is known as 'viscose.' Its uses depend upon the ease with which the cellulose can be regenerated from the solution and in any desired form, viz. compact solid ('viscoid'), sheet or film, powder, or lastly thread ('lustra-cellulose') — retaining in these forms the essential properties of the original fibrous cellulose.

* Neue Gesichtspunkte zur Theorie der Colloids. E. Jordis, Erlangen, 1904. Researches on Cellulose, **2**. Cross and Bevan.

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Viscose is used in the engine sizing of pulps for working up into paper and boards; in the coating of papers as the vehicle, chiefly for white pigments such as barium sulphate and China clay; in the preparation of filmed fabrics such as 'leather cloths'; and for a number of other similar purposes.

These applications all depend upon the relatively low cost of production of this particular solution of cellulose, together with the obvious advantages of an aqueous solution from which cellulose is directly regenerated by a variety of simple methods.

Cellulose and Acid Radicals: Cellulose Esters. For the reasons previously given, these compounds will only be briefly described, i.e. only so far as is necessary to complete our review of the general chemistry of cellulose. While these derivatives are many of them of enormous industrial importance, they have only an indirect connection with the work of the paper-maker, and for further information we must refer him to special treatises.

An ester may be generally defined as a species of salt formed by union of an alcoholic OH group with an acid, water being formed and eliminated. In these reactions cellulose may be represented by its unit group $C_6H_{10}O_5$.

The introduction of acid groups in the place of the alcoholic hydroxyl groups of the cellulose takes place, however, in stages which graduate from the minimum to the maximum degrees of substitution by such minute increments that observers have been forced to the conclusion that the reactions are practically continuous. The question of the maximum number of OH groups in the $C_6H_{10}O_5$ unit which are replaceable by acids is still a matter of controversy, but it is generally conceded that at least three of the groups can be so substituted.

The lower esters are formed from the fibrous celluloses without disintegration; the higher acetates and nitrates are produced by alternative processes, that is, (1) with conservation of the fibrous form, the structural details persisting in the products; (2) the fibres are structurally more or less attacked and gelatinised under esterification. The result, either (2) or (1),

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depends on whether the medium in which the reaction takes place is or is not a solvent of the product. The esters of monovalent acid groups are differentiated from the parent cellulose, not only by specific relation to solvents, but by a diminished attraction for atmospheric moisture proportional to the degree of esterification.

The following particulars of the several groups of esters will serve to indicate their general characters and relations.

Nitric Esters: Cellulose Nitrates.—These are the best known of the synthetical derivatives of cellulose, their discovery dating back over fifty years, during which period they have come into ever-increasing industrial application. They are formed by the inter-action of cellulose, in any form, and concentrated nitric acid. Water being formed simultaneously, it is usual to carry out the reaction in the presence of sulphuric acid, which combines with and removes the water from the sphere of reaction.

Until recently it has been thought that the influence of the sulphuric acid was limited to its direct function of 'fixing' water. But it is now proved to take a direct part in the reaction (Cross and Bevan, 'Researches on Cellulose,' ii., p. 51), and residues of SO_4 groups in combination with the cellulose, are a main cause of instability of the crude nitrates as industrially prepared [they are removed by prolonged washing and boiling with water; the nitrates are then stable].*

Apart from this complication, the cellulose nitrates may be prepared by direct interaction of cellulose and concentrated nitric acid, and a concise view of the entire series of those of the nitrates thus prepared is given by Vieille, in a paper entitled 'Sur les degrés de la Nitrification limites de la Cellulose.'† From the title of this author's communication, it may be concluded that it is a study of the nitrations of cellulose (cotton) under the condition of progressive variations, with the view of determining the maximum fixation of the nitric group corresponding to such variations. The most im-

* Robertson, Journ. Soc. C.I., 1906, 624.
† Compt. Rend. **95**, 132.

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portant factor of the process is the concentration of the nitric acid, which was the variant investigated. The temperature was kept constant—11° C.—and the nitrating acid (nitric acid only) was employed in very large excess (100–150 times the weight of cellulose), so as to avoid disturbance of the results by rise of temperature or by dilution of the acid. The products were analysed by Schlœsing's method, and the analyses are expressed in c.c. NO (gas) (at 0° and 760 mm.) per 1 grm. of substance.

In regard to the time factor, or duration of exposure to the acid required to give the maximum number, this was in cases controlled by observation. Thus with the acid $HNO_3, \frac{1}{2}H_2O$ (1·488 sp. gr.), after 48 hours the product was still blued by iodine, and gave 161 c.c. NO; whereas after 62 hours' exposure the iodine reaction was not obtainable, and the maximum

Sp. gr. of acid.	Composition (approximate).	Analysis of Product c.c. NO per 1 grm.	Properties of Products.
1·502 1·497	$NO_3H.\frac{1}{4}H_2O$	202·1 197·9	Structural features of cotton preserved; soluble in acetic ether; *not* in ether-alcohol $C_{24}H_{20}(NO_3H)_{10}O_{10}$
1·496 1·492 1·490	$NO_3H.\frac{1}{3}H_2O$	194·4 187·3 183·7	Appearances unchanged; soluble in ether-alcohol; collodion cotton $C_{24}H_{22}(NO_3H)_9O_{11}$ $C_{24}H_{24}(NO_3H)_8O_{12}$
1·488 1·483	$NO_3H.\frac{1}{2}H_2O$	165·7 164·6	Fibre still unresolved; soluble as above, but solutions more gelatinous and thready $C_{24}H_{26}(NO_3H)_7O_{13}$
1·476 1·472 1·469	$NO_3H.\frac{2}{3}H_2O$	140·5 140·0 139·7	Dissolve cotton to viscous solution; products precipitated by water; gelatinised by acetic ether; *not* ether-alcohol $C_{24}H_{28}(NO_3H)_6O_{14}$
1·463 1·460 1·455 1·450	$NO_3H.H_2O$	128·6 122·7 115·9 108·9	Friable pulp; blued strongly by iodine in KI solution; insoluble in alcoholic solvents $C_{24}H_{30}.(NO_3H)_5O_{15}$ $C_{24}H_{32}(NO_3H)_4O_{16}$

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number (165·7 c.c. NO) was obtained. At the slightly lower gravity 1·483, an exposure of 120 hours was necessary. At the still lower gravity when the cotton (nitrate) passes into solution, the maximum is very rapidly attained (5 minutes).

The highest nitrate obtained as above, with nitric acid only, is somewhat lower than when sulphuric acid is present. Under these latter conditions the author regards the highest nitrate obtainable as $C_{24}H_{18}(NO_3H)_{11}O_9$.

Several well characterised nitrates are known, but it is a very difficult matter to prepare any one in a state of purity, and without admixture of a higher or lower nitrated body.

A recent exhaustive study of the nitrates produced under the conditions of the ordinary industrial processes, with the mixed acids (H_2SO_4 and HNO_3) has been made by G. Lunge, and for further study students are referred to the original.*

By the graduated action of alkaline hydrates on the nitrates previously dissolved, hydroxypyruvic acid is obtained as a main product. (W. Will.)

Technical Applications.—The nitrates of cellulose, as such, are the basis of extremely important industries, and of very opposite character, viz. (1) the production of explosives both for military and industrial use, and (2) as a structural material in the production of xylonite and celluloid, both in the form of compact solids and in sheet or film. The latter uses depend upon the ease with which the nitrates are brought into a plastic condition, or entirely dissolved in various 'neutral' solvents, e.g. alcohol-ether, acetone, amyl acetate. In association also with camphor and vegetable oils (castor oil) their plastic qualities are considerably heightened.

In later years the nitrates have been used as a means of obtaining an artificial cellulose fibre: the solutions of the nitrate are drawn or spun into the air or into water as a precipitating medium, and the thread is afterwards 'denitrated' by treatment with magnesium sulphide solution. The resulting product is a nearly nitrogen-free cellulose. It is known

* J. Amer. Chem. Soc., 1901, **23**, 527. See also 'Researches on Cellulose,' 1906, Cross and Bevan, pp. 30–70.

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as artificial silk, or by the more appropriate term, lustra-cellulose.

Cellulose Acetates.—Certain of the polyhydric alcohols, e.g. glycerin, unite directly with acetic acid to form acetic esters. Both starch and cellulose have been recently shown to react with glacial acetic acid at the boiling point of the latter.* With acetic anhydride the reaction proceeds to a higher limit, and the monoacetate (C_6 unit) is readily formed. This ester is formed without sensible structural modification. The monoacetate is insoluble in all simple solvents, and resists the action of the special solvents of cellulose, e.g. cuprammonium (p. 9).

When cellulose is heated with the anhydride at elevated temperatures about 160°, the higher acetates are formed, and dissolve to highly viscous solutions.

For the industrial production of these higher acetates, the anhydride may be made to react at lower temperatures (below 50° C.) in presence of sulphuric acid, which acts as catalyst. As in the case of the nitrates, there is a direct reaction with fixation of SO_4H residues, which are, however, replaced for the most part by the acetyl groups.

The triacetate is readily produced under these conditions of reaction, with reduced proportions of reagents and in approximately quantitative yields.

The acetates are compounds of critical importance in regard to the question of the constitution of cellulose. Investigations have indicated that the acetylation may proceed to a higher limit, viz. to tetracetate—but the analytical results have been called in question,† and the matter requires further investigation.

Technical Applications.—The acetates give highly colloidal solutions in special solvents, of which the most satisfactory is chloroform. The esters are recovered in any desired form, e.g. as film, or as thread or in masses. The most important application of the acetates is for coating fine wires used in electrical

* Cross and Traquair, Chem. Ztg, 1905, No. 39.

† A. G. Green, Ztschr. f. Farb. in Textil Chem., **3**, 97, 309. Green and Perkin, J. Chem. Soc., 1906, **89**, 811.

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instruments, its use depending upon high insulation, and low inductive capacity.

Its employment as fibre or artificial silk, is limited by considerations of cost.

One of the most characteristic acetylations of cellulose is the following: The cellulose regenerated from the thiocarbonate is, after purification, mixed with the molecular proportion of zinc or magnesium acetate [$C_6H_{10}O_5 : Zn(O.C_2H_3O)_2$] in concentrated solution, the mixture dried down on the water-bath, and finally dehydrated at 105°. It is then moistened with acetic anhydride, and acetyl chloride is added in the proportion of $2.C_2H_3O.Cl$. Reaction ensues at 30–50°, the mass liquefies, and the formation of the cellulose acetate results. The pure product is obtained as an opaque, white, voluminous powder, soluble in acetic acid and chloroform, to solutions of high viscosity which, on evaporation in thin layers, leave the acetate in the form of transparent coherent film. On boiling these films with normal sodium hydrate diluted with an equal volume of alcohol, the ester is resolved into acetic acid (soluble as sodium acetate) and cellulose (insoluble). The cellulose is obtained as a transparent coherent film. This is an important criterion of a true cellulose acetate, as distinguished from acetates of derivatives of lower molecular weight; the latter giving brittle films which are more or less disintegrated by the process of saponification, and also yield a proportion of soluble carbohydrates, reducing cupric oxide in alkaline solution.

Technical Applications.—The acetates have only recently been prepared on the manufacturing scale. Their physical properties are very similar to those of the nitrates; they are, however, non-explosive and withstand a temperature of 200°. It appears, therefore, that they are capable of substituting the nitrates in many of their useful applications other than as explosives, and with greatest advantage when the properties of an explosive or high inflammability are not merely superfluous but prejudicial.

Cellulose Benzoates.—Esters containing the radical of benzoic acid are obtained by inter-action of the alkali celluloses

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with benzoyl chloride in presence of excess of the solution of alkaline hydrates.

(*a*) *Mercerised Cellulose.*—The benzoates obtained from the alkali cellulose in this form retain the fibrous structure of the original cellulose. A mixture of products is obtained, varying in composition from a mono- to di-benzoate.

(*b*) *Soluble Alkali Celluloses.*—These react in a more definite way: the products are purified by dissolving in glacial acetic acid, filtering from residues of unattacked cellulose, and reprecipitating by water. Thus isolated, the benzoates approximate in composition to $C_6H_8O_3{<}^{O.C_7H_5O}_{O.C_7H_5O}$, i.e. to di-benzoate. The benzoates have been but little studied, and at present they have a purely theoretical interest.

Cellulose-Sulphuric Acids (*Esters*).—The solution of cellulose in concentrated sulphuric acid is attended by combination, which may be formulated as under :—

$$C_6H_8O_3{}^{(OH)}_{(OH)} + {}^{H.SO_4H}_{H.SO_4H} = {}^{H_2O}_{H_2O} + C_6H_8O_3.(SO_4H)_2.$$

The compound is described by Stern*—the author of the most recent contributions to the subject—as 'cellulose' disulphuric ester; but it has not been determined that the compound is a true cellulose derivative. It is more than probable that the original cellulose molecule is simultaneously resolved. The compound may be isolated in the form of its barium salt, $C_6H_8O_3(SO_4)_2Ba$, which is insoluble in alcohol. The formation of a derivative of this formula is the first stage in a complicated process of resolution of cellulose, which in many respects resembles that of starch by hydrolytic agents. The ultimate product in both cases is dextrose. The interaction of cellulose and sulphuric acid plays an important indirect part in various processes of esterification, such as the production of the cellulose nitrates by treating cellulose with mixtures of nitric and sulphuric acids, and in the formation of the acetates by treating cellulose with acetic anhydride in presence of sulphuric acid

* A. L. Stern, Journ. Chem. Soc., 1895, 1, 74–90.

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(p. 34) and acetic acid. The sulphuric acid in these reactions plays the part of catalyst, and, while combining with the OH groups of the cellulose, is in turn expelled by the mono-hydric acid radicals.

This substitution is, however, not complete, and residues of SO_4H are fixed in both the nitrates and the acetates.

The fact is of considerable importance in reference to the technical uses of these products. Cellulose nitrates (gun cottons) containing these residues, show special instability and sensitiveness to heat, and the industrial process of preparation which involves a prolonged series of boilings with water for purification. 'Stabilisation' is in great measure determined by the necessity of eliminating these residues.

Mixed Esters.—From the above discussion it will be evident that various derivatives of cellulose can be produced containing more than one acid radical. A series of aceto-sulphates has been prepared by the authors with J. F. Briggs.*

The mixture of acetic-anhydride and acetic acid in equal proportions, containing increasing quantities of sulphuric acid up to 8 p.ct. gives a series of mixed aceto-sulphates, graduating into higher members, which are water-soluble.

Aceto-nitro-sulphates have also been prepared, and, again, by treating the benzoates with nitric acid, mixed nitro-benzoates are formed, and a nitric group also enters the benzoyl residue. These mixed esters have the general characteristics of the simple esters, and will be found fully described in 'Researches on Cellulose,' i. and ii.

Constitution of Cellulose.—What we have now set forth with regard to the typical cellulose as a chemical individual, is the basis of all we can be said to know of its actual constitution. The empirical facts exhibit a close similarity to those which characterise starch as a chemical individual; both have the empirical formula $n\,(C_6H_{12}O_6 - H_2O)$; both give synthetical derivatives (esters) having similar structural relationships to the original; both are resolvable into monose (hexose) groups by processes of hydrolysis, direct or indirect. But these

* Berl., Ber. 1905, pp. 38 and 1859.

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analogies soon break down when we come to examine into the behaviour of these compounds as chemical individuals in being. Starch is particularly sensitive to hydrolytic agents, such as the enzymes, or soluble ferments, by which it is resolved into a highly complex series of soluble hydrates, dextrins, maltose, dextrose. Cellulose, on the other hand, may be taken through cycles of profound changes of synthesis and decomposition without change of weight.

Typical instances of this extraordinary resistance of cellulose are the cycle of processes by which it is converted into an artificial lustrous thread, thus :—

Nitrate Process: Stage I.—Conversion into nitric ester, combining with 60–70 p.ct. of its weight of HNO_3.

Stage II.—Conversion of the dissolved nitrate into thread.

Stage III.—Removal of the combined NO_3 by processes of denitration.

Viscose Process: Stage I.—Conversion into alkali cellulose by combination with 50 p.ct. of its weight of sodium hydrate, and thereafter into sulphocarbonate by interaction with carbon bi-sulphide.

Stage II.—Conversion of the dissolved xanthate into thread by continuous coagulation.

Stage III.—Processes of fixing (acid) and purifying. These two cycles of conversion and reversion present the sharpest of contrasts of chemical conditions with the common feature of the conservation of the cellulose.

It must also be conceded, both in the experimental chemical facts and the relations of visible structure to composition, that the reactions involved are, in effect, continuous.

Whereas it is usual to express chemical reactions by stoichiometrical molecular formulæ and equations, which express the quantitative relations of the ultimate reacting units, without reference to intermediate mass-relationships, it appears that the latter have an objective significance in the case of cellulose. Cellulose is, in fact, an aggregate, and reacts as such, and its reactions are best interpreted by regarding this aggregate much in the same way as a solution—that is, a complex made up in

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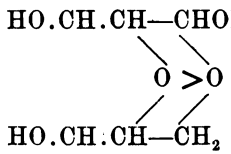
part of molecules more or less 'associated,' and of dissociated residues or 'ions.'

The type of 'solution' here implied is that of a saline electrolyte in water; and there are many features of the reactions of cellulose which are those of an amphoteric electrolyte. Cellulose, in fact, in presence of water, is a conductor of electricity, and in transmitting the current becomes the arena of characteristic electrolytic phenomena such as to justify its description as an intrinsic electrolyte.

Lastly, we have to deal with cellulose as a typical colloid, and to note that the theories of the colloidal state, which are in course of evolution through observations of various members of this heterogeneous group, are generalisations of conclusions of a similar order.

The problem of the constitution of cellulose is, therefore, not merely that of formulating a unit molecular group, consistent with the reactions of synthesis, as well as expressing the fact that it may be decomposed into monoses of C_6 dimensions, or other immediate derivatives.

A. G. Green has proposed, loc. cit., a formula of this order, which has a value as a general expression—



But it must not be forgotten that such formulæ may be entirely misleading if interpreted as a revelation of the actual condition of matter in the cellulose aggregate.

It would convey a false impression to attempt to represent the constitution of cellulose more closely. In systematic chemistry, a constitutional formula is justified by the synthesis of the compound from components of known structure: this criterion is necessarily wanting in the case of cellulose, as it is also in that of starch. The synthesis of both compounds has so far only been observed in or by the living cell. Two simple cases of cellulose synthesis of this order may be noted, in

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which its formation takes place directly from the crystallisable sugars.

(1) As a result of a change which is set up 'spontaneously' in beet juice, a white insoluble substance is formed and separated in lumps or clots: this substance has all the characteristics of cellulose. After separating this substance, the solution gives with alcohol a gelatinous precipitate resembling the hydrates of cellulose previously described.*

(2) The 'vinegar plant' takes a membranous form which, under microscopic examination, is seen to be clearly differentiated from the zoogloea form of the *Bacterium Aceti*,† and to which the name of *B. Xylinum* has been given. It is, in fact, composed of bacterial rods of 2 μ length contained in a membranous envelope. This envelope has the properties and composition of cellulose. Pure cultures of the organism placed in solutions of levulose, mannitol and dextrose reproduce the growth in question, i.e. of the bacteria enveloped in a 'collecting medium' of cellulose. The proportion of cellulose formed to the soluble carbohydrate disappearing, is highest in the case of levulose. The cellulose, however, when hydrolysed by sulphuric acid, gives a dextro-rotary sugar. This fact contains a suggestion that the oxygen in cellulose is of ketonic type or function.

Up to the present, in the outline which we have given of the chemistry of the typical cellulose, we have been chiefly concerned with its OH groups; considered broadly, we have studied the compound from the one aspect of its relationship *to water*. As a substance playing an enormously preponderating part in the plant world, its relationship *to oxygen*, i.e. generally to oxidising agents, is of equal importance, since the chemistry of our planet is obviously a 'water and oxygen' chemistry.

We note, in the two succeeding sections, the more important destructive actions determined by oxidising agents and water (hydrolysis).

Decompositions of Cellulose by Oxidants. — It has been already pointed out that cellulose is comparatively

* E. Durin, Compt. Rend., **82**, 1078; **83**, 128.
† A. J. Brown, Journ. Chem. Soc., **49**, 432.

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resistant to the action of oxidants; that most of the processes for isolating or purifying (bleaching) cellulose depend, *per contra*, upon the use of oxidising agents, which readily attack the 'impurities' with which it is combined or mixed in raw fibrous materials. The cellulose resists the action of these oxidising agents, and, further, withstands in a high degree the action of atmospheric oxygen. It is this general inertness of the compound which marks it out for the unique part which it plays in the vegetable world and in the arts.

It must be again noted that this high degree of resistance to hydrolysis (alkaline) and oxidation belongs only to cotton cellulose and to the group of which it is the type, and which includes the celluloses of flax, rhea and hemp. A large number of celluloses, on the other hand, are distinguished by considerable reactivity, due to the presence of 'free' CO groups, and are therefore more or less easily hydrolysed and oxidised. The 'celluloses' of the cereal straws and esparto grass are of this type, and hence the relative inferiority of papers into the composition of which they enter.*

On the other hand, we have now to study those processes of oxidation to which it yields more or less readily.

A. Oxidation in Acid Solutions.—(1) *Nitric acid* (1·1–1·3 sp. gr.) attacks cellulose at 80–100°, at first slowly then more rapidly, but tending to a limit at which the action again becomes very slow. This limit corresponds with the formation of a characteristic product of oxidation—*oxycellulose*. This substance, which is white and flocculent, when thrown upon a filter and washed with water, combines with the latter to form a gelatinous hydrate. It requires, therefore, to be rapidly washed with dilute alcohol. It amounts to about 30 p.ct. of the cellulose acted upon, the remainder being for the most part completely oxidised to carbonic and oxalic acids. On ultimate analysis it gives the following numbers:—

$$\left.\begin{matrix} C & 43\cdot4 \\ H & 5\cdot3 \end{matrix}\right\} C_{18}H_{26}O_{16}.$$

It dissolves in a mixture of nitric and sulphuric acids, and on

* Journ. Chem. Soc., 1894, 472.

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pouring into water, the nitrate $C_{18}H_{23}O_{13}(NO_3)_3$ separates as a white flocculent precipitate. From the low number of OH groups reacting with the nitric acid, it may be concluded that the compound is both a condensed as well as an oxidised derivative of cellulose. This oxycellulose dissolves in dilute solutions of the alkalis, and on heating the solutions they develop a strong yellow colour. Warmed with concentrated sulphuric acid it develops a pink coloration similar to that of mucic acid. The compound exhibits generally a close resemblance to the pectic group of colloid carbohydrates.

The by-products of this oxidation are carbonic and oxalic acids, together with the lower nitrogen oxides. The solution, examined at any stage, appears to contain traces only of intermediate products of oxidation of the cellulose. The reaction is divisible into the two stages: (1) the conversion of the cellulose into hydracellulose, evidenced by its breaking down to a fine flocculent powder; and (2) the oxidation of the hydracellulose.

The oxycelluloses resulting from this process differ from those formed by the action of CrO_3 (*infra*), in giving small yields only of furfural (2–3 p.ct.) on boiling with HClAq (1·06 sp. gr.). It is also to be noted that the carbon is higher than that of the oxycelluloses, giving large yields of furfural (p. 50). These points suggest that, side by side with oxidation, combination of the negative oxy-groups with the more basic groups of unattacked molecules takes place, giving derivatives of the nature of esters. And, indeed, the reaction may be even more complicated. It is clear, from the composition of the nitrate, that the proportion of basic OH groups is reduced to a minimum.

The reaction requires further systematic research in the light of our increased knowledge of the constitution of the simpler carbohydrates and the simple products of their oxidation.

(2) *Chromic acid*, in dilute solutions, attacks cellulose with extreme slowness; in presence of mineral acids oxidation proceeds more rapidly, but at ordinary temperatures is still very slow. The action is, therefore, easily controlled within any desired limit, the oxidation being in this case, of course,

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directly proportionate to the amount of CrO_3 presented to the fibre. The oxidation is accompanied by disintegration, and the insoluble product is an oxidised cellulose, or oxycellulose, the yield and composition of which bear a simple relation to the amount of oxidation to which the cellulose is subjected. Its properties are similar to those of the oxycellulose above described. It dissolves in a diluted mixture of sulphuric and hydrochloric acids (57 p.ct. H_2SO_4, 5·5 p.ct. HCl), and on diluting and distilling with HCl of 1·06 sp. gr., is decomposed with formation of furfural, $C_4H_3O.COH$, the yield of this aldehyde being proportionate to the state of oxidation of the product.

This is illustrated by the subjoined results of observations :—

Weight of cellulose.	CrO_3 employed.	Yield of oxycellulose.	Yield of furfural p.ct. of oxycellulose.
4·7	1·5	93·0	4·1
4·7	3·0	87·0	6·3
4·7	4·5	82·3	8·2

(Berl. Ber. 26, 2520.)

The first effect of treatment with CrO_3 appears to be that of simple combination ; reduction to the Cr_2O_4 then ensues, and the further deoxidation requires the presence of a hydrolysing acid.

From the statistics of the reaction it appears there is little 'destruction' of the cellulose ; and, as the oxidation is not attended by evolution of gas (CO_2), we may assume that the reaction consists simply in oxidation with the fixation of water. A certain proportion of the products are dissolved by the acid solution, and of the insoluble residue (oxycellulose) a large proportion is easily attacked and dissolved by alkaline solutions. The product is no doubt, therefore, a mixture ; and, indeed, it would be hardly conceivable that an aggregate like cellulose should be equally and simultaneously attacked.

The reaction is so perfectly under control that it must be regarded as giving a regulated dissection of the molecule of cellulose, and therefore is an especially attractive subject for exhaustive investigation.

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The carbohydrates of low molecular weight are similarly oxidised by chromic acid, and the product of oxidation similarly resolved with formation of furfural.

It is to be noted with cellulose, as with the carbohydrates of low molecular weight, that by oxidation its equilibrium is disturbed in such a way that carbon condensation is easily determined. This fact is of physiological significance, and will be referred to subsequently.

(3) *Of other acid oxidations* which have not been particularly investigated, we may mention the action of Cl gas in presence of water, of hypochlorous acid, and of the lower oxides of nitrogen in presence of water. Generally the result of these treatments is similar: the formation of insoluble products having the properties of the oxycelluloses above described, and soluble products which are oxidised derivatives of carbohydrates of low molecular weight. These, however, are usually obtained in relatively small quantity.

Atmospheric oxidation of cellulose—if it could be proved to take place—would fall in this category, as cellulose surfaces under ordinary conditions of exposure would be found to be normally acid. From the evidence we have of the condition of paper and textiles of the flax group after centuries of exposure to ordinary atmospheric influences, we may conclude that the oxidation of the normal celluloses under these conditions is excessively slight.

B. Oxidations in Alkaline Solution.—(1) *Hypochlorites*, in dilute solution (< 1 p.ct.) and at ordinary temperatures, have only a slight action upon cellulose—a fact of the highest technical importance, since hypochlorite of lime (bleaching powder) is the cheapest of all soluble oxidising compounds, and the most effective oxidant of the coloured impurities which are present in the raw cellulose fibres or formed as products of alkaline hydrolysis.

While the normal celluloses withstand these bleaching oxidations, there are many celluloses widely differentiated from the cotton type which are eminently oxidisable, and, at the same time, susceptible of hydrolysis. The 'celluloses' of esparto and

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straw are of this kind (see p. 52), and the economic bleaching of paper pulps prepared from these raw materials can hardly be expected to follow upon the same lines as that of 'rag' pulp (cotton and linen). A study of the factors involved in the process will be found in a paper entitled 'Some considerations in the Chemistry of Hypochlorite Bleaching.'* These factors are—in addition to temperature and concentration (Cl_2O) of the bleaching solution—the nature of the base in union with the hypochlorous acid, and its proportion to the acid. A knowledge of the operation of these factors will enable the bleacher to control a process which is usually carried out on an entirely empirical basis.

The resistance of cellulose to the action of these solutions necessarily has its limits, and when these are exceeded the fibre-substance is oxidised and disintegrated, and an oxycellulose results. These effects are rapidly produced by the joint action of hypochlorite solutions and carbonic acid. The oxycellulose formed in this way acquiring the property of selective attraction for certain colouring matters—notably the basic coal-tar dyes—its presence in bleached cloth is easily detected by a simple dyeing treatment consisting in immersing the oxidised fabric in a dilute solution (0·5–2·0 p.ct.) of one of these dye stuffs, e.g. methylene blue. Local over-oxidation may be diagnosed in this way with certainty, and bleachers' damages may be thus ascertained, and often traced back to the operating cause in the light of this 'oxycellulose' test.†

The oxycellulose or disintegrated fibre resulting from this process of oxidation differs but little in empirical composition from cellulose itself, probably owing to the fact that the more highly oxidised products are dissolved in the solution of the oxidant, which is, of course, basic. Its reactions indicate the presence of free CO groups, and it readily undergoes further oxidation by atmospheric oxygen, the oxidation being much accelerated by temperatures over 60°. The OH groups of this oxycellulose are also more reactive than those of the original cellulose.

* Journ. Soc. Chem. Ind. 1890. † Ibid.. 1884.

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The facts in relation to the conversion of cotton cellulose into oxycellulose by the action of bleaching powder were first made known by Georges Witz* in 1883.

Since then a number of papers have been published dealing with special aspects of the phenomena—theoretical and practical. Of these we may cite : Schmidt, Dingl. J. 250, 271 ; Franchimont, Rec. Trav. Chim. 1883, 241 ; Nölting and Rosenstiehl, Bull. Rouen, 1883, 170, 239 ; Nastjukow, Bull. Mulhouse, 1892, 493.

It is probable on many grounds that the oxidised products obtained from cellulose by the action of the hypochlorites in the manner described are mixtures of one or more oxycelluloses with residues of unoxidised cellulose. More recent investigation has led to the conclusion that the extreme product of oxidation is an oxycellulose of the empirical formula $C_6H_{10}O_6$, which is freely soluble in dilute alkaline solutions in the cold ; and that cellulose oxidised by hypochlorite solutions is a variable mixture of this product with hydracellulose, and unaltered cellulose. (Nastjukow.)

By drastic oxidation of cellulose by the oxyhalogen compounds—i.e. by treatment with chlorine or bromine in presence of alkaline hydrates—the complex is entirely broken down to the simplest products. With bromine, i.e. hypobromite, some quantity of bromoform is obtained ; carbon tetrabromide is also easily obtained and identified.†

(2) *Permanganates.*—The permanganates in neutral solution attack cellulose but slowly, and they may therefore be usefully employed as bleaching agents. In presence of alkalis a more drastic oxidation is determined. The degree of oxidation is, of course, dependent upon the conditions of treatment. The following general account of a particular experiment and its results will illustrate its main features.

22·6 grms. cellulose, with 400 c.c. caustic soda solution ; 50 grms. $KMnO_4$ added in successive small portions ; tempera-

* Bull. Soc. Ind. Rouen, **10**, 416 ; **11**, 169.
† Collie, Journ. Chem. Soc. **65**, 262.

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ture, 40–50°. Proportion of cellulose to oxidising oxygen, $2C_6H_{10}O_5 : 7O$.

The main products were—

(α)	Oxycellulose . .	10·5 grms.,	approximately	50 p.c.
(β)	Oxidised carbohydrates in solution . .	3·5 „	„	16 „
(γ)	Oxalic acid . . .	4·3 „	„	20 „
(δ)	Carbonic acid, water and traces of volatile acids	. . .	„	14 „

(α) The oxycellulose gelatinised on washing and was similar to the product obtained by the action of nitric acid.

(β) The oxidised carbohydrate in solution resembled 'caramel' in appearance. The compound or mixture was precipitated by basic lead acetate, and isolated by decomposing the precipitate with hydrogen sulphide, filtering and evaporating. On distillation from hydrochloric acid, furfural was obtained in large proportions.

(3) *Extreme action of Alkaline Hydrates.*—When fused at 200–300° C. with two to three times its weight of sodium or potassium hydrates, cellulose is entirely resolved, the characteristic products being hydrogen gas and acetic (20–30 p.ct.) and oxalic (30–50 p.ct.) acids. Generally the reaction takes the same course as with the simpler carbohydrates, resolution of the cellulose into molecules of similar constitution, no doubt, preceding the final resolution; with certain stages the reactions are exothermic or even explosive.

C. Destructive Resolution by Ferment Actions.—This group of decompositions of cellulose is necessarily a very wide one. In the 'natural' world of living organisms, of course, no structures are permanent; and although cellulose distinguishes itself by relative permanence and resistance to the disintegrating actions of water and oxygen, the differentiation in this respect is only a question of degree, and all cellulosic structures are subject to the law or necessity of redistribution.

The directions of redistribution are chiefly three: viz. (1) In the assimilating processes of the plant a cellulosic structure is broken down, re-absorbed into the supply of plastic nutrient material, and re-elaborated.

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(2) Structures which have ceased to play a part in the general organisation of the plant are cast off, and then exposed as 'dead' matter to the play of the redistributing agencies of the natural world. The processes of 'decay' take various forms, according to the conditions to which they are exposed. The humus of soils, peat, lignite, and all forms of coal present various forms of the residual solid products of the decay of cellulosic structures, the remainder having been dissipated and restored to the general fund of matter in circulation, in the gaseous form—viz., as CO_2 and CH_4.

(3) In the processes of animal nutrition plants and vegetable substances are, of course, most important factors. In the course of animal digestion the vegetable substances are attacked by the fluids of the alimentary tract and resolved into proximate constituents fulfilling the requirements of the organs of assimilation; and, in addition to these decompositions, which are largely hydrolytic in character, more fundamental resolutions are observed in which the carbohydrate molecules are completely broken down, i.e. with formation of gaseous products.

The Cellulose Group.—Thus far we have been dealing mainly with one member of the very numerous class of plant constituents comprehended in the term 'cellulose.' While the properties and characteristics of cotton cellulose are in such wise representative that this substance may be regarded as the typical cellulose, the differentiation of this, as of every other group of tissue constituents, in conformity with functional variation, necessarily covers a wide range of divergencies.

The celluloses of the plant world, so far as they have been investigated from the point of view of chemical constitution, group themselves as follows :—

(*a*) Those of maximum resistance to hydrolytic action, and containing no directly active CO groups.

(*b*) Those of lesser resistance to hydrolytic action, and containing active CO groups.

(*c*) Those of low resistance to hydrolysis, i.e. more or less soluble in alkaline solutions and easily resolved by acids, with formation of carbohydrates of low molecular weight.

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GROUP (*a*).—In addition to the typical cotton cellulose—which, it is to be noted, is a seed-hair—there may be included in this group the following fibrous celluloses which constitute the bast of exogenous flowering annuals: viz. the celluloses of *Flax* (Linum usit.), *Hemp* (Cannabis sativa), *China Grass* (Rhea and Boehmeria species), and of the lesser known Marsdenia tenacissima, *Calotropis* (gigantea), *Sunn Hemp* (Crotalaria juncea).

As in the case of cotton, the celluloses of the fibres are considered in the form of the white (or bleached) and purified residues, resulting from the treatment of raw materials by processes of alkaline hydrolysis and oxidation more or less severe in character. For the purification of the celluloses in the laboratory, the methods usually practised consist in (1) alkaline hydrolysis, i.e. treatment with boiling solutions of sodium hydrate, carbonate or sulphite; (2) exposure to bromine water or chlorine gas; or, when oxidation alone is sufficient for the removal of the 'impurities,' to solutions of the hypochlorites or permanganates (in the latter case followed by a treatment with sulphurous acid to remove the MnO_2 deposited on the fibre substance); (3) repetition of (1) for the removal of products rendered soluble by (2).

The celluloses of this group thus purified may be taken as chemically identical with cotton cellulose, investigation having so far failed to differentiate them. It must be noted, however, that the several members of the group present distinct morphological characteristics, and differ also in such external properties as lustre and 'feel.' These are correlated with the differences in minute structure, but they are no doubt in part due to differences of substance. So far, however, we have no knowledge of the proximate constitution of these substances, and can therefore say nothing as to the causes of difference in this respect.

On the other hand, the essential identity of these celluloses is established in regard to ultimate composition and in reference to the following properties and reactions:—

(1) Resistance to hydrolysis and oxidation, and other negative characteristics, indicating non-reactivity of the CO and low reactivity of the OH groups.

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(2) The relationships to the special solvents previously described, including the thiocarbonate reaction.

(3) Formation of water-insoluble esters, nitrates, acetates, benzoates.

Of the above, it is sufficient in general laboratory practice to examine cellulose in regard to ultimate composition, resistance to alkaline hydrolysis, behaviour with solvents, and reactions with sulphuric acid (solution without blackening) and nitrating mixture (H_2SO_4 and HNO_3); the 'nitration' proceeds without oxidation, and gives a high yield of product, 160–180 p.ct., according to the conditions.

GROUP (*b*).—These celluloses are differentiated from the former group (1) by ultimate composition, the proportion of oxygen being higher; (2) by the presence of active CO groups; (3) in certain cases by the presence of the $O.CH_3$ group.

The general characteristics are those of oxidised and partially hydrolysed celluloses. It has recently been shown that these oxidised derivatives of the normal celluloses are further characterised by yielding *furfural* as a product of acid (HCl) decomposition. The yield of this aldehyde is, in certain cases, increased by previous treatment of the oxycellulose with a reagent prepared by saturating sulphuric acid of 1·55 sp. gr. with HCl gas. In this reagent the oxycelluloses dissolve; and on then diluting with HCl of 1·06 sp. gr. and distilling, maximum yields of furfural are obtained, the yield being an indirect measure of the increased proportion of oxygen beyond that corresponding with the formula $C_6H_{10}O_5$.

Celluloses of this class are much more widely distributed in the plant world than those of the cotton type; they appear, from recent observations, to constitute the main mass of the fundamental tissue of flowering plants, in which they usually exist in intimate mixture or combination with other groups more or less allied in general characteristics. It appears, from a survey of the contributions of investigators to the subject of cellulose, that research has been very much confined to the fibrous celluloses, more particularly to such as receive extended industrial use. The time has come, however, when systematic

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research is much needed to establish at least a preliminary classification of the 'cellular' celluloses upon the lines of chemical constitution. Constitution, taken in relation to physiological function, is an attractive subject of research; and it is in the plant cell, where synthetical operations are predominant, that we have to look for the foundations of a 'new chemistry,' which shall definitely investigate the relation of matter to life.

It is to be noted that the differentiation of many of these celluloses from the typical cotton is, in regard to empirical composition, only slight. There appear, on the other hand, to be more important differences of constitution. Thus pine-wood cellulose dissolved in sulphuric acid, the solution diluted and boiled, and further treated for the isolation of crystallisable carbohydrates, yields these (i.e. dextrose) in only small proportions.*

Investigation has stopped short at this negative result. It would be of interest, therefore, to isolate the products formed in the reaction with the concentrated sulphuric acid, so as to characterise them, at least generally. Until this is done, or some other method of proximate resolution is worked out in detail, we can only say that the constitution of these celluloses is in some important feature radically different from that of the typical cellulose.

An account of recent investigations of these 'celluloses' will be found in Berl. Ber. 1893, and a more special treatment of the subject, *ibid.* 1896, 1457, and Journ. Chem. Soc. 1894–1898 (C. Smith).

Of this group of the natural oxycelluloses, the following have been more particularly investigated:—

(1) *Celluloses from woods and lignified tissues generally.*—Lignified tissues are made up of compound celluloses, to be subsequently described (see 'Ligno-celluloses,' p. 56), from which the celluloses may be isolated by a number of treatments, all depending upon the relative reactivity of the so-called 'non-cellulose' constituents, which in combination with the

* Lindsey and Tollens, Lieb. Ann. **267**, 370.

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celluloses constitute the compound cellulose, ligno-cellulose or wood-substance. These non-cellulose constituents are readily attacked and converted into soluble derivatives; and there are various industrial processes for preparing celluloses (paper pulp) from raw materials of this class, depending upon the direct conversion of the former into such soluble compounds. The isolated celluloses show the following general characteristics:*—

Elementary composition { C 42·8–43·8 p.c. / H 5·6– 5·9 „ } *Yield of furfural*, by solution and decomposition (HCl) 2–6 p.c. *Reactions* with phenylhydrazine salts and magenta-sulphurous acid, indicating the presence of active CO groups. These celluloses are necessarily less resistant to oxidation and hydrolysis, but show in all other respects a close general agreement with the normal cotton cellulose.

(2) *Celluloses from Cereal Straws, from Esparto, etc.*—These celluloses are isolated from the matured stem or haulm, by digestion with alkaline lye at elevated temperatures. They are also of considerable industrial importance, being largely used in the manufacture of the cheaper kinds of writing and printing papers.

Recent investigation has shown that these celluloses are strongly differentiated from the normal, and generally resemble the oxycelluloses. The following are the characteristics of difference:—

Ultimate composition, after treatment with hydrofluoric acid, to remove siliceous ash constituents:—

	Oat straw cellulose.		Esparto cellulose.	
	(1)	(2)	(1)	(2)
C . . .	42·4	42·4	41·78	41·02
H . . .	5·8	5·8	5·42	5·82

Yield of furfural by solution and decomposition (HCl):—

Oat straw cellulose.	——	Esparto cellulose.
12·5		12·2

Reactions.—In addition to those with Fehling's solution,

* Berl. Ber. 27, 161.

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phenylhydrazine salts, and magenta-sulphurous acid indicating the presence of active CO groups, the celluloses give a characteristic rose-red colouration on boiling with solutions of aniline salts. This reaction serves to identifiy their presence in papers, and from the depth of the colouration the percentage may be approximately estimated.

Investigation has also established the following points in regard to the oxidation and deoxidation of these celluloses.

They are gradually oxidised in dry air at the temperature of the water-oven, undergoing discoloration; the yield of furfural by hydrolysis showing a progressive increase. They are deoxidised, on the other hand, by neutral and alkaline reducing agents. Thus, after lengthened exposure to solutions of zinc-sodium hyposulphite, prepared by the action of zinc dust upon sodium bisulphite, the yield of furfural—which is a measure of the degree of oxidation—was reduced, in the case of esparto cellulose, from 12·6 to 8–9 p.ct.

A certain deoxidation results from solution of these oxycelluloses as thiocarbonate, and regeneration of the cellulose by heating the solution at 80–100°. The regenerated cellulose approximates to the normal, yielding 2–3 p.ct. furfural on hydrolysis. It is to be noted, however, that esparto cellulose, in common with all the celluloses of this group, is partly hydrolysed to soluble derivatives by this treatment; the regenerated cellulose amounting to 80 p.ct. of the original weight dissolved. The soluble portions yield furfural on hydrolysis, amounting (in a typical experiment) to 4·0 p.ct. of the original.

The celluloses of this group are dissolved by concentrated sulphuric acid to dark-coloured solutions. On diluting and boiling, they are resolved into carbohydrates of low molecular weight; dextrose appears to be invariably formed, and in many cases also mannose; but only very small yields of either carbohydrates have been so far obtained.

Group (*c*).—This includes the heterogeneous class of non-fibrous celluloses which we have defined as of low resistance to hydrolysis, being easily resolved by boiling with dilute acids, and being also more or less soluble in dilute alkaline solutions.

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This group has been but little studied and therefore can only be generally characterised. Physiological research has shown that there are a large number of cellular, as distinguished from fibrous 'celluloses,' which are readily broken down (hydrolysed) by the action of enzymes within the plant itself, whether as a normal or abnormal incident of growth. Thus, in the germination of starchy seeds, the cell walls (cellulose) of the starch-containing cells are broken down, as a preliminary to the attack upon the starch granules themselves, to form the supply of nutrition to the embryo. In an exhaustive investigation of the germination of barley, Brown and Morris have thrown a good deal of light upon this particular point, which they emphasise in the following words: 'that the dissolution of the cell wall invariably *precedes* that of the cell contents during the breaking down of the endosperm is a fact of the highest physiological importance, and one which for the most part has been strangely overlooked.'

A similar, but abnormal, dissolution of cell walls is that which occurs in the attacks of parasitic organisms upon the tissues which they invade.

These processes are well known to physiologists, who, however, generally regard 'cell wall' and 'cellulose' as substantially identical terms. The chemical differentiation of the substances comprising cell walls is, on the other hand, an entirely new field of research; but, although investigation has not gone very far, the results are sufficient to show that the celluloses of this order are widely diversified. The variations already disclosed are (1) those of carbohydrates yielded by ultimate hydrolysis, and (2) those of molecular configuration and actual constitution. We have already seen that the celluloses of the cotton group (*a*) yield dextrose as the ultimate product of hydrolysis; those of group (*b*) yield, in addition to dextrose, mannose and probably other bodies; and the group we are at present discussing yield, in addition, galactose, and the pentoses xylose and arabinose. In illustration we may cite a few examples. Thus GALACTOSE has been obtained as a product of hydrolysis of the cell walls of the seeds of Lupinus luteus, Soja

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hispida, Coffea arabica, Pisum sativum, Cocos nucifera, Phœnix dactylifera, etc. MANNOSE is obtained in relatively large quantity from the 'ivory nut,' and from a very large number of other seeds; and PENTOSES, from the seeds of the cereals and of leguminous plants. It appears, therefore, generally that a large number of plant constituents which have been denominated by the physiologists as 'cellulose' have little more title to be considered as such than has starch. However, external resemblances count for something, at least in the beginnings of classification, and substances of the type we are considering may be conveniently grouped with the celluloses; but we may apply to them the term PSEUDOCELLULOSES, or HEMICELLULOSES—as has been proposed by E. Schulze. Our group (*c*) of pseudo-celluloses may therefore be defined as substances closely resembling in appearance the true celluloses, but easily resolved into simple carbohydrates by the hydrolytic action of enzymes, or of the dilute acids and alkalis.

Compound Celluloses.—In dealing with the isolated celluloses, it has been shown that the processes by which they are isolated or purified are based upon the relative reactivity of the compounds with which the celluloses are combined or mixed, in the raw or natural products of plant life. These natural forms of cellulose are, of course, multitudinous. Remembering the infinite variety of the vegetable world, the endless differentiation of form and substance of the tissues of plants, it might be presumed that the chemical classification of these products would present unusual complications.

Investigation, however, has shown, and continues to show, that this great diversity of substance, as revealed by proximate analysis, exists upon a relatively simple chemical basis. The compounds constituting the fundamental tissue of plants may, in fact, be broadly classified in correspondence with the three main types of differentiation of the cell wall long recognised by the physiologists, viz. *lignification*, *suberisation* and conversion into *mucilage*. That is to say, in addition to the celluloses proper and hemi- or pseudo-celluloses—which may be defined as polyanhydrides of the normal carbohydrates, ketoses and

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aldoses—there are three main types of *compound* celluloses in which the celluloses as thus defined exist in combination with other groups, as follows :—

LIGNOCELLULOSES.—The substance of lignified cells and fibres, notably the woods—of which the characteristic *non-cellulose* constituent is a cyclo-hexene derivative.

PECTOCELLULOSES AND MUCOCELLULOSES.—Comprising a wide range of tissue constituents—of which the non-cellulose constituents are colloidal forms of the carbohydrates, or closely-allied derivatives, easily converted by hydrolytic treatments into soluble derivatives of lower molecular weight, and belonging to the series of 'pectic' compounds, or hexoses, etc.

ADIPOCELLULOSES AND CUTOCELLULOSES.—The substance of cuticular and suberised tissues—in which the cellulose is associated with fatty and waxy bodies of high molecular weight.

Of the above groups, the first only has any direct interest to the paper-maker. The ligno-celluloses *as such* are, in the forms of the jute fibre and 'mechanical' pulps, actual components of papers of certain classes; the pectic and cuticular constituents of fibrous raw materials are almost entirely eliminated by the chemical and mechanical methods of treatment of such materials, for separating and preparing the actual paper-making fibres.

LIGNOCELLULOSES.—As the chemical prototype of the substance of lignified tissues, we select the jute fibre. This fibre is the isolated bast of plants of the species Corchorus (order *Tiliaceæ*) an annual of rapid growth, attaining a height of 10–12 feet in the few months required in the Indian climate for the maturing of the plant. The textile fibre or bast is obtained in long strands. It is of a brown to silver-grey colour in the finer sorts.

The jute *fibre substance* differs strikingly in composition and reactions from the celluloses. Its ultimate composition is represented by the percentage numbers :—

		Calc. for $C_{12}H_{18}O_9$.
C	46·0–47·0	47·0
H	6·1– 5·8	6·0
O	47·9–47·2	47·0

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The above numbers are calculated to dry ash-free substance. In the air-dry condition the fibre contains on the average 10·0 p.ct. moisture; the normal ash amounts in the aggregate to about 1·0 p.ct.

Reactions.—It is differentiated from the celluloses by the following characteristic reactions. With solutions of salts of *aniline* (and analogues) it gives a deep yellow colouration, with *dimethyl-p.-phenylene diamine* a deep red colouration. With *phloroglucinol* dissolved in hydrochloric acid (1·06 sp. gr.) it gives a rose-red colouration; the red solution of *ferric ferricyanide* (p. 96) is reduced with production of 'Prussian' blue which is deposited in the fibre-substance; a solution of *magenta* decolorised by *sulphurous acid* dyes the fibre a deep magenta colour, a reaction which is characteristic of aldehydes and ketones. The jute fibre is also dyed directly by a large variety of the 'coal tar' dyes.

But the most characteristic of its reactions is that of direct combination with the halogen elements, and notably chlorine. The combination is attended with change of colour to bright yellow; the yellow quinone chloride (*infra*) is dissolved by a solution of sodium sulphite, with development of a magenta-red colouration.

While serving thus as a qualitative reaction for the identification of the lignocellulose, it is also one which takes place in definite quantitative proportions. Further, when so carried out, it affords a sharp separation of the lignocellulose into its constituent groups: viz. (1) the *lignone* (ketone) which combines with the chlorine and may then be dissolved away by sodium sulphite solution, leaving (2) the *cellulose* constituents of the fibre-substance, having the properties of the celluloses of group (2) of the classification on p. 48.

From its critical importance, the process of chlorination of the jute lignocellulose will be described in detail. The fibre is prepared by a preliminary treatment with a boiling solution of sodium hydrate (1 p.ct. NaOH). From this it is well washed and squeezed to retain not more than its own weight of water. In this condition it is exposed for one hour

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to an atmosphere of washed chlorine gas. The fully chlorinated fibre is washed to remove the hydrochloric acid formed in the reaction, and transferred to a solution of the sulphite (1–2 p.ct. Na_2SO_3) in which it is boiled. To complete the isolation of the cellulose, the solution is made alkaline with sodium hydrate (0·2 p.ct. NaOH), after which the boiling is continued 2–3 minutes. The fibrous mass is thrown on a cloth filter, and thoroughly washed. This residue is the almost pure *cellulose*; and the entire elimination of the *non-cellulose* components of the original fibre, is shown by failure to react with the various reagents previously cited.

The following are important quantitative data. The yellow chlorinated derivative has the empirical formula $C_{19}H_{18}Cl_4O_9$; to form this derivative the fibre-substance (purified and prepared by the boiling with alkali) takes up 8 p.ct. of its weight in *combination*; at the same time an equal amount goes to form hydrochloric acid. The proportion of cellulose yielded is approximately 80 p.ct. This cellulose is a mixture of two celluloses, *α cellulose*, resembling the normal cotton cellulose, and *β cellulose*, a furfural-yielding cellulose, and much less resistant to hydrolytic treatments, both acid and alkaline. In other processes of attacking the fibre for the isolation of cellulose, this latter is hydrolysed and dissolved, and the yield falls to 62–66 p.ct.

Bromine acts similarly, but its action is relatively slow and incomplete. Thus, if the fibre prepared by boiling in weak alkalis is submerged in saturated bromine water, it requires some hours at the ordinary temperature for the fibre-substance to combine with the maximum proportion of the halogen. The brominated product is similarly attacked and dissolved by alkaline solutions; but it will be found that the treatment requires to be once or twice repeated before the isolation of cellulose is complete. In certain cases, however, the method is useful as an alternative process of isolating and estimating cellulose, not only in jute, but in other fibrous materials.

Iodine is absorbed by the lignocelluloses from aqueous

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solutions, and they are coloured a deep brown. The absorption is constant, under constant conditions of treatment, and, as a result of quantitative investigations, it was established that in digesting the fibre-substance at 18° C., with twenty times its weight of the $\frac{N}{10}$ iodine solution (in potassium iodide) the absorption is constant at 12·9–13·3 p.ct.

No definite compound is formed, however, and the halogen is easily removed by solvents.

These reactions with the halogens, and notably with chlorine, are dealt with thus prominently, as they are specifically characteristic of the lignone or non-cellulose group, the presence of which in combination with the cellulose is the distinguishing feature of this class of compound celluloses. The lignone group is sharply differentiated from the carbohydrates by its reactions, which are those of an unsaturated compound. Investigation of the chlorinated derivative has established it as a *quinone chloride*, and related to the trihydric phenol pyrogallol, as it yields trichloropyrogallol on reduction. Subordinate characteristics of the lignone complex are the presence of methoxyl groups ($O.CH_3$), and the small proportion of reactive hydroxyl (OH) groups. It must be noted that the union of cellulose and lignone to form the ligno-cellulose complex is very intimate, and in several characteristic reactions, both of decomposition and synthesis, the ligno-cellulose behaves as a homogeneous compound. Of such we may cite more particularly the actions of hydrolytic agents under ordinary conditions, on the one hand, and reactions of 'nitration' and 'acetylation' on the other. The highly reactive nature of the lignone group exposes it, on the other hand, to selective attack not only by the halogen as described, but by dilute nitric acid at temperatures of 50° and upwards, and by sulphurous acid and the bisulphites at elevated temperatures, all leading consequently to the isolation of the more resistant cellulose.

We must briefly note here the structural relationship of the jute-cellulose to the jute-fibre. The cellulose is obtained in the form of single, ultimate, bast fibres or cells, of short

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length (2 mm. = $\frac{1}{12}$ inch); whereas, the jute-fibre occurs in apparently long strands. The latter are, however, in effect complex, and a cross-section viewed under the microscope reveals a number of the unit cells in close apposition. It would appear therefore that these fibre-bundles owe their cohesion to the *lignone* constituent; and hence the term '*incrusting and intercellular substance*' by which it is frequently designated. This view is at variance with the undoubted chemical homogeneity of the fibre-substance; and the student must avoid any so crude a view of a lignocellulose, as of pure cellulose 'overlaid' or 'incrusted' with its lignone or non-cellulose components.

The remaining features of the chemistry of the typical lignocellulose we note only briefly.

Action of Cellulose Solvents.—The lignocellulose is attacked and dissolved similarly to the celluloses, by zinc chloride in concentrated solution, whether in water or hydrochloric acid: so also by solutions of cuprammonium. The solution is attended by hydrolysis, which is greater or less according to the conditions and duration of the action: by precipitation of the solutions the recovery of the lignocellulose is therefore incomplete. The lignone groups are found in both soluble and insoluble fractions.

Action of Hydrolytic Agents.—(1) *Alkaline solutions* at temperatures of 60–100° attack the lignocellulose as a whole, dissolving a proportion of the fibre-substance from 10–25 p.ct., according to the nature of the alkali, the concentration of the solution and the temperature and duration of its action. With caustic soda solution (of 3 p.ct. Na_2O) at elevated temperatures (150–170°), the lignone and β cellulose groups are selectively attacked, and a cellulose is isolated approximating in composition to the normal celluloses.

Concentrated solutions of caustic soda (12–25 p.ct. Na_2O) in the cold determine a 'mercerising' action, attended by a remarkable change in appearance due to partial resolution of the fibre-bundles, and the swelling of the individual fibres. These hydration effects are accompanied by a partial conversion

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into soluble derivatives (10–15 p.ct.) but there is no essential change in the composition of the lignocellulose.

(2) *Acids.*—The dilute 'mineral' acids, e.g. HCl and H_2SO_4 of semi-normal strength rapidly disintegrate the fibre at temperatures exceeding 60°. As the action continues the fibre takes a mahogany-red colour and falls to a mass of brittle fragments, harsh to the touch. The acid solution acquires a reddish-yellow colour and smells strongly of acetic acid: this acid is in effect produced in some quantity. The furfural-yielding groups of the lignocellulose yield more readily to these actions, and when the lignocellulose is digested with 1 p.ct. sulphuric acid at 3 atm. pressure, they are entirely hydrolysed and dissolved. The insoluble fibrous residue gives the characteristic reactions of the original fibre, i.e. the essential features of its lignone constituent are not changed.

Dilute Nitric Acid at 50–80° has a specific and selective action upon the lignone group; from which soluble yellow coloured nitroso-ketonic acids are formed, the β cellulose is simultaneously hydrolysed, and finally the α cellulose is isolated. The reaction is characteristic, and has been more closely studied with the related group of lignocelluloses, the hard woods.*

Compounds with Acid Radicals. *Sulpho-carbonate Reaction.*—The joint and simultaneous action of carbon disulphide, and the alkaline hydrates e.g. solutions of 15–20 p.ct. NaOH, produces only a partial converson of the constituents of the fibre into sulpho-carbonates, the proportion actually passing into solution on subsequent treatment with water varying from 25–50 p.ct. according to the conditions of treatment. The reaction is remarkable for the extreme degree of hydration and gelatinisation of the portion which does not actually dissolve: in the swollen and gelatinised condition it has been observed to occupy 100 times the volume of the original. In this reaction it is the group we have designated as β cellulose which yields most readily, and is in fact, dissolved. The undissolved residue reacts with chlorine as does the original lignocellulose.

* E. C. C. Baly and J. C. Chorley, Berl. Ber. 1895, 922.

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Water-Insoluble Esters. *Esters.*—Of these, the nitrates are alone of sufficiently definite composition to be considered as derivatives of the entire lignocellulose.

The nitrates are obtained by short exposure to the action of the mixed acids ($HNO_3 + H_2SO_4$); with concentrated nitric acid alone, rapid and destructive oxidation supervenes. The highest yield of nitrate obtainable has been determined at 145 p.ct. of the original lignocellulose: this increase of weight would correspond with the production of a tri-nitrate of the formula $C_{12}H_{15}O_6.(NO_3)_3$. The percentage of nitrogen in the products is from 11·8 to 12·2, and this indicates the production of a tetra-nitrate. This discrepancy is accounted for by secondary reactions—with production and removal of water molecules. The nitrates are of a brilliant yellow colour and are homogeneous in composition, fractional solution failing to resolve them, as would be the case if they were mixtures of cellulose nitrates, with derivatives of the lignone group. In explosive properties, and in their behaviour towards solvents, they closely resemble the cellulose nitrates.

Compounds with other acid radicals, e.g. acetates and benzoates, have been obtained, but they are of an ill-defined character.

Action of Oxidising Agents.—As 'unsaturated' compounds, i.e. containing unsaturated groups, the lignocelluloses are relatively greedy of oxygen. Also it is evident that the lignone groups yield more readily to such actions than the cellulose constituents of the fibre. Thus by the action of chromic acid in dilute solution and in presence of sulphuric acid, the former may be entirely eliminated. The most important oxidations, however, are those of the 'standard' bleaching agents—the permanganates and hypochlorites. By a careful regulation of the conditions, the jute fibre may be bleached by these reagents to a very high point, but by no means to the pure white of a cellulose. The *lignocellulose* is essentially a coloured compound, and in attempting to exceed the limit which this imposes, we merely remove the lignone groups and approximate to the condition of cellulose. This implies loss of

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weight, and for the reasons given above, loss of strength by actual disintegration of the fibre-bundles.

As the products of oxidation of the fibre substance are acid in character, precautions must be taken in employing the hypochlorites, that the bleaching solutions do not become acid: in that case hypochlorous acid is set free and the lignone groups are *chlorinated*. The presence of the resulting chlorinated derivatives in paper or textiles is extremely prejudicial.

The lignocelluloses, of which we have briefly described the typical jute-fibre, are of course widely distributed in the plant world, and are the components of structures of various function. We may instance as lignocelluloses of closely related composition and constitution, the hard or stony concretions of the pear: and, again, the most important constituent of the juice of the white currant, a type of soluble and hydrated lignocelluloses, of which group it has all the essential characteristics. This latter is a further proof that the lignocelluloses, though complex, are homogeneous. But the most widely distributed of the lignocelluloses are the woods: in this group a surprising unity of chemical type is preserved; and though a woody stem is made up of cells and vessels of various structure and function, we may regard them as composed of an identical chemical substance. In the woods proper, all those features of the typical lignocellulose, which it has in contrast to cellulose, are more strongly developed. This is readily seen by a comparison of a typical wood, viz. beech-wood, with the jute-fibre in regard to the essential chemical constants:—

—	Elementary Composition.	Proximate resolution.		Quantitative Reactions of Non-cellulose.		
	Carbon.	Cellulose.	Non-cellulose.	Methoxyl.	Furfural.	Cl. Combining.
Jute .	46·5	75	25	4·0	8·0	8·0
Beech .	49·1	55	45	6·0	12·8	12·0

Remembering that the woods are the substances of perennial stems, whereas the lignocelluloses previously dealt with occur

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in or as 'annual' structures, these numbers contain the suggestion that the process of *lignification* consists chemically in the production of the unsaturated lignone groups at the expense of cellulose. This view is emphasised by the progressively 'condensed' character of the union of the groups, which shows itself in the relatively strong resistance of the woods to all processes of simple hydration and hydrolysis. This is most clearly seen in relation to the solvents of cellulose: for while jute and the 'annual' lignocelluloses are similarly dissolved, the woods yield to no process of solution as a whole. More definitely characteristic is their complete resistance to the thiocarbonate reaction; which argues the absence of reactive OH groups. This, again, is confirmed by the results of conversion into nitrates by the action of nitric acid in presence of sulphuric acid, which are so imperfect and unsatisfactory that this group of lignocelluloses cannot be said to be 'nitrated' as such, but yield only as the result of partial resolution into constituent groups. A little reflection will show that inertness in these directions is an important condition of such 'permanent' functions as the woods are destined to fulfil.

But in all other respects there is the closest similarity between the two groups of lignocelluloses. The specific colour reactions are shown by the woods in greater intensity proportioned to their higher proportion of unsaturated (lignone) groups, thus:—

(*a*) Golden yellow, with solutions of salts of aniline, an intense red with dimethyl-p.-phenylene diamine.

(*b*) Carmine-red, with solutions of phloroglucinol in HCl (1·06).

(*c*) Magenta, due to liberation of this colouring matter from its solutions decolorised by sulphurous acid.

(*d*) Prussian blue, 'reduced' from solutions of ferric ferricyanide.

Further, the characteristic reactions with chlorine and bromine, due to their combination with lignone groups.

The reaction with solutions of *dimethyl-paraphenylene-diamine* we may mention more particularly, as it is the basis

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of a method of estimating the proportion of these *lignocelluloses* in a paper. The woods are prepared by a *mechanical* process of wet grinding, for working up into papers of a certain kind and quality (p. 151), in which therefore they are present in their 'natural' or undecomposed form. With this particular base they give a deep red colouration; and in any mixture with a substance such as cellulose giving no such reaction, the depth of colour is proportional to the percentage of the lignocellulose in the mixture. With a series of standard mixtures, i.e. of known composition, a comparison is at once instituted determining the composition of a given specimen. This test was devised by C. Wurster, who further simplified it by preparing test papers containing the reactive base which are moistened and pressed upon a sample to be tested. The colour developed is compared with a scale of chromo-printed stripes representing the colour produced with 10, 20 . . . . 100 p.ct. of the lignocellulose.

We have seen that the condition of combination of these constituent groups prevents the woods reacting as a homogeneous compound. The chemistry of these substances, therefore, is based chiefly on a study of their decompositions, of which the most important are those which yield the cellulose in a pure form. We give, therefore, a brief survey of these processes.

Laboratory Methods. (1) ACTION OF HALOGENS.—The wood is prepared in fine shavings, boiled out in dilute alkaline solutions (1 p.ct. NaOH), washed and exposed to chlorine gas or saturated bromine-water in the cold. The resulting compound of lignone and halogen is dissolved away by a solution of sodium sulphite as described on p. 58. The treatment is repeated until a pure cellulose is isolated.

A series of determinations by Hugo Müller gave the following percentages of cellulose in representative woods :—

—	Birch.	Beech.	Ebony.	Oak.	Poplar.	Fir.	Pine.
Cellulose p.ct.	55·5	45·5	30·0	39·5	62·8	53·3	57·0

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(2) Joint Action of Halogen and Nitric Acid. *Schultze's Method.*—The wood is digested 10–14 days in the cold, with nitric acid of 1·10 sp. gr. to which potassium chlorate is added. The lignone is attacked jointly by chlorine and nitrogen oxides, and largely converted into derivatives soluble in the acid solution, the residues being removed by treatment with dilute ammonia. This process is unsatisfactory as a quantitative method, but is a useful illustration of the characteristics of the unsaturated lignone groups.

(3) Dilute Nitric Acid at 60–80°.—The wood is digested with excess of the acid of (5–7 p.ct. HNO_3). As a result of complicated reactions comprising hydrolysis, oxidations, combination of lignone groups with lower nitrogen oxides, and destruction of these by further action of nitrous acid, a pure cellulose is finally obtained. The chemistry of the process is fully dealt with in a paper previously cited.*

Industrial Processes.—The above methods are not employed on the industrial scale, chiefly because the reagents are too costly. The manufacturers' methods of obtaining a cellulose pulp from wood all consist of hydrolytic treatment at high temperatures, of which the underlying principles will appear from the following considerations.

(1) Action of Water and Dilute Acids.—The action of water at elevated temperatures brings about a partial hydrolysis, but the conversion into soluble products rapidly reaches a limit determined by the opposing tendency to further condensation of the constituent groups of the lignocellulose. This is aided by the strongly acid character of the dissolved products. The results are very similar, in fact, to those obtained with the dilute mineral acids (HCl, H_2SO_4). These actions have recently been exhaustively studied by Simonsen, who has revived the idea of employing waste wood (sawdust, etc.) treated in this way as a source of fermentable sugars. By this process the yield of 'sugar' amounts to 17–24 p.ct. of the wood, of which three-fourths yields to yeast fermentation. The yield of alcohol is 6–7 litres (absolute) per 100 kilos of wood.†

* Berl. Ber., 1895, 922.

† See E. Simonsen, Ztschr. f. Angew. Chem. 1898 [**42**] 962-966; [**44**] 1007-1012.

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(2) Action of Alkalis.—Since the woods tend to break down under hydrolytic treatment with production of acid bodies, it is obvious that in the presence of alkalis, the limit of hydrolysis will be much extended. In fact, by employing the alkaline hydrates the decomposition proceeds to a virtual isolation of cellulose (in the form of the ultimate wood cells), the non-cellulose or lignone being almost entirely converted into soluble products.

The conditions of the 'soda process' of wood boiling are, a digestion of 7–10 hours at 90–100 lbs. steam pressure with a lye of 11–15° B.

The 'Sulphate' Process is only a variation of the above, sulphate of soda being used as the chief source of the alkali, being reduced to sulphide in the after-process of evaporating and igniting with the organic matters, dissolved from the wood (in a previous digestion).

(3) Sulphurous Acid and Bisulphites.—We have already seen that certain acid treatments enable us to entirely decompose the lignocellulose with isolation of cellulose—these depending upon an entire destruction of the lignone groups, i.e. to products of very low molecular weights. The ketonic character of the lignone groups exposes them, on the other hand, to a selective attack by sulphurous acid. In the presence of this acid condensation of hydrolysed ketones is prevented, and under suitable conditions, which were determined as an industrial process by Raoul Pictet, this acid entirely resolves the lignocellulose into insoluble cellulose and soluble derivations of the non-celluloses, differing but little in chemical condition from that in which they occur in the original wood. This decomposition takes place at 80–100° with solutions of the acid containing 5–7 p.ct. SO_2.

But this process has ceded in industrial importance to those in which the bisulphites of the alkaline earth-metals are used as the decomposing agent. In these processes the wood, after suitable mechanical preparation, is digested for many hours at elevated temperatures with solutions of calcium or magnesium bisulphite. In such a process it is easy to see that the hydrolysis and solution of the lignone constituents

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of the wood is due (1) to the action of the 'free' sulphurous acid; (2) to the tendency of aldehydic and ketonic CO-groups to combine with bisulphites, as formulated below:—

$$R.HCO + MH.SO_3 = R.HC(OH)MSO_3;$$

and (3) to a development of the latter reaction in cases where (as in the lignone groups) the carbonyls are combined with unsaturated residues. To take as an illustration an aromatic aldehyde of known constitution, cinnamic aldehyde, $C_6H_5.CH:CH.CHO$, which forms with sodium bisulphite, first the additive compound $C_8H_8O.NaHSO_3$, which on heating with the bisulphite undergoes a change to the *sulphonic acid*, $C_6H_5.CH_2.CH(SO_3Na).CHO$.

From an exhaustive investigation of the soluble by-products of the process, the following points have been established—that the lignone groups are dissolved with very slight constitutional change; that in solution they have the characters of sulphonated derivatives; that, however separated into fractions, these all have an identical composition, viz. that represented by the formula $C_{24}H_{23}(OCH_3)_2O_7.SO_3H$, again showing that the lignone constituents, though complex, are definite and homogeneous compounds; that the sulphonated derivatives still contain CH = CH groups, and yield brominated products of formula $C_{24}H_{22}(OCH_3)_2Br_4SO_9$.

(4) NEUTRAL SULPHITES.—It may be mentioned as of theoretical interest, that solutions of the normal alkaline sulphites also determine a complete resolution of the wood into cellulose (insoluble) and lignone derivatives; but owing to the feeble hydrolysing action of these salts, the reactions require higher temperatures. They partake of the characters of both the acid (bisulphite) and alkali processes, differing from the latter by minimising the secondary changes of the dissolved products.

In the table on the following page a general view of these processes is given, with names of the pioneer inventors and dates from which 'public knowledge' of the processes may be considered as beginning.

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View of the Chemical Processes for Disintegrating Wood.

Aqueous Alkalis.

Hydrolysis, aided by alkali directly, also indirectly by combination with products of resolution. — Watt and Burgess, 1853. Houghton, 1857.

Solutions of Alkaline Sulphides.

Hydrolysis aided by alkaline bases directly and indirectly by combination with products. Reversal of hydrolysis lessened by presence of reducing agent. — Jullion, 1855. Blitz, 1883. Dahl, 1884.

Water.

Hydrolysis, aided by acids formed from the wood. — Fry, 1867.
Limit of action determined by reversal of hydrolysis, i.e. dehydration aided by oxidation.

Water, together with neutral Sulphites.

Simple hydrolysis—
Products removed from sphere of action by combination with base and sulphite. — Cross, 1880.
Oxidation prevented by presence of sulphite.

Aqueous Acids.

(*a*) Oxidising and hydrolytic—
Nitric acid. — Coupier and Mellier, 1852. Barre and Blondel, 1861.
Nitro-hydrochloric. — Orioli, 1865.

(*b*) Simply hydrolytic—
Hydrochloric acid. — Bachet and Machard, 1864.

(*c*) Reducing and hydrolytic—
Sulphurous acid. — Tilghmann, 1866. Pictet, 1882.

Bisulphites.

Hydrolysis, aided primarily by sulphurous acid, and secondarily by combination of products with bisulphites, also by prevention of oxidation. — Tilghmann, 1866. Mitscherlich, 1874. Ekman, 1881. Francke, 1881. Graham, 1882.

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Pecto-Celluloses.—This second group of the compound celluloses will require very brief treatment—for the reason that they are not employed *as such* as paper-making materials.

The *pectic group* of plant compounds are a group of gelatinisable 'carbohydrates' widely distributed in the less permanent of vegetable structures. The general relationships of the group, as determined by the earlier observers, are these: *Pectose*, the insoluble mother-substance of the group, occurs in mixture or union with the cellulose of the parenchyma of fleshy fruits and roots, e.g. apples, pears, turnips, etc. This is hydrolysed by boiling dilute acids or alkalis, or by a ferment enzyme (pectase) secreted in the tissue, to *pectin* ($C_{32}H_{48}O_{32}$, Frémy), the solutions of which readily gelatinise. By continued hydrolysis (boiling water) this is further modified to parapectin, and by alkalis to metapectin and parapectic acid and pectic acid ($C_{32}H_{44}O_{30}$, Frémy; $C_{12}H_{16}O_{11}$, Regnault; $C_{12}H_{16}O_{10}$, Mulder; $C_{14}H_{22}O_{14}$, Chodnew).

The final product of hydrolysis is metapectic acid. To this acid Frémy assigned the formula $C_8H_{14}O_9$. Later investigations have established its general identity with arabic acid—a complex acid which is the main constituent of gum-arabic. Gum-arabic yields, on graduated hydrolysis, a complex of glucoses (galactose, arabinose) and a series of arabinosic acids, e.g. $C_{23}H_{38}O_{22}$, and compounds differing from this by $+ C_6H_{10}O_5$. It appears, therefore, generally, that the pectic group are compounds of carbohydrates of varied constitution with acid groups of undetermined constitution, associated together to form molecular complexes, more or less homogeneous, but entirely resolved by the continued action of simple hydrolytic agencies; and the *pecto-celluloses* are substances of similar character, in which the carbohydrates are in part replaced by *non-hydrolysable celluloses*. The general characteristics of the *pecto-celluloses* are therefore these: they are resolved by boiling with dilute alkaline solutions into *cellulose* (insoluble) and soluble derivatives of the *non-cellulose* (pectin, pectic acid, metapectic acid); they are gelatinised under the alkaline treatment; they are 'saturated compounds,' not reacting with the

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halogens, nor containing any groups immediately allied to the aromatic series.

It should be noted that the later researches of Tollens* have thrown doubt on the conclusions of Frémy and the earlier observers as to the acid character of these 'pectic' substances. Careful analysis of a wide range of 'pectins' showed that the $H_2 : O$ ratio characteristic of the carbohydrates proper, is equally characteristic of many pectins; whereas the presence of acid groups would mean a higher oxygen ratio. It may also be noted that it is difficult to distinguish the pectins proper from the hemi- or pseudo-celluloses (see p. 55).

Generally, therefore, by a pecto-cellulose we mean a compound or intimate mixture of a cellulose with colloidal carbohydrates, or their derivatives readily hydrolysed by both acids and alkalis to simpler soluble forms. Compound celluloses of this kind are enormously diversified in composition, structural character, and distribution, and the group, having none of the sharp lines of differentiation and demarcation presented by the lignocelluloses, cannot be handled at all in the same way.

We must confine ourselves, therefore, to the one or two more definite types which have been investigated.

Flax.—Commercial flax is a mixed product. The bast fibre proper constitutes from 20–25 p.ct. of the entire stem, and is more or less imperfectly separated from the wood on the one side, and the cortical tissue-elements on the other, by the ordinary processes of retting and scutching. These residues are visible with the naked eye, but are brought into clearer evidence by means of reagents, followed by microscopic examination. Thus the *wood* is an ordinary lignocellulose, and gives the characteristic reactions; the *cortical tissue* is again distinguished from the fibre proper by reacting strongly with magenta-sulphurous acid. The presence of the cortical tissue is also marked by the large proportion of 'oil and wax' constituents present in the fibre (3–4 p.ct.). Excluding these adventitious constituents, the fibre proper is a pecto-cellulose. That the non-cellulose constituents of flax are pectic compounds was first established

* Annalen, **286**, 278.

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by Kolb.* According to his observations, the precipitate obtained on acidifying the alkaline solutions from the 'boiling' of flax goods consists of pectic acid.

The proportion of these constituents varies from 14–33 p.ct. in the different kinds of flax, the variations being in part due to the plant, i.e. to physiological habit and conditions of growth; in part to the different methods of retting the plant—and extracting the fibre. After well boiling with the dilute alkali (1–2 p.ct. NaOH) the fibre substance consists of flax cellulose, with residues of the wood (sprit), cuticular tissues, and oils and waxes associated with the latter. By exposure to chlorine (after well-washing and squeezing) the wood is attacked in the usual way, and is then easily resolved by alkaline treatment. To purify the cellulose it requires to be boiled out with alcohol, and finally treated with ether-alcohol to remove the oil-wax residues. In this way flax cellulose is isolated in the laboratory in an approximately pure condition. It might appear from the outlines of this laboratory method that the bleaching of flax goods, which consists substantially in the isolation of the pure flax cellulose, is a comparatively simple process. This is not so, however. The exigencies of economical and safe treatment of textile fabrics prescribe certain narrow limits of chemical treatment; and the removal of the more resistant wood (lignocellulose) and cuticle (cuto-celluloses) under these conditions involves a reiterated round of treatments consisting of—

Alkaline hydrolysis .	Boiling in solutions of NaOH, Na_2CO_3, etc.
Oxidation . .	Hypochlorite solutions and atmospheric oxidation (grassing).
Souring . . .	Treatment with dilute acids in the cold.

It must be remembered, however, that the problem is not the removal of the non-cellulose constituents of the fibre itself —these disappear almost entirely in the earliest alkaline treatments—but of compound celluloses of the other two main groups.

The further investigation of the pectose of flax fibre has

* Bull. Soc. Ind. Mulhouse, June 1868.

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not been prosecuted according to the methods of later years. Such investigations will, no doubt, be undertaken in due course.

FLAX CELLULOSE has been mentioned incidentally to the general treatment of the celluloses. So far no reactions have been brought to light in which it is differentiated from cotton cellulose, with perhaps one exception, viz. its lesser resistance to hydrolysis. Thus H. Müller mentions * that flax cellulose, isolated by the bromine method, lost, on boiling five times with a dilute solution of sodium carbonate (1 p.ct. Na_2CO_3), 10 p.ct. of its weight. The statements of R. Godeffroy,† that flax cellulose is distinguished from cotton cellulose by its reducing action upon silver nitrate in boiling neutral solution, are erroneous, the reaction resulting from residual impurities, which for the reasons given, are extremely difficult to isolate. Flax cellulose may therefore, for the present, be regarded as chemically indistinguishable from cotton cellulose.

The oil and wax constituents of the raw fibre will be described under the group of *cuto-celluloses*.

OTHER PECTO-CELLULOSES.—As far as investigation has proceeded, it appears that pectose, or pectose-like substances, are associated with all fibrous tissues of the unlignified order. And indeed in the lignocelluloses themselves pectous substances make their appearance with increasing age. Thus the lower portions of the isolated jute bast—jute cuttings or butts—when boiled in alkaline solution yield products which cause the solution to gelatinise on cooling; and the gelatinous product is insoluble in alcohol, distinguishing it, as pectic acid, from the products of hydrolysis of the lignocellulose itself, which are dissolved, after precipitation, by alcohol. It must be remembered, however, that in the 'jute cuttings' the adhesion of the bark and cortical parenchyma to the true bast fibre is such that we are dealing with a complex tissue, and the source of the pectic acid may be in the parenchyma of the tissue and not in the bast fibre. On the other hand, it has been

* Pflanzenfaser, p. 38.
† Abstracted in Journ. Soc. Chem. Ind. (1889), 575.

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shown that in the spontaneous decomposition of jute, lying in the damp state, gelatinous acid bodies are formed indistinguishable from pectic acid. It would not be difficult, therefore, to account for the pectic constituents of the bast tissue towards the root end as products of degradation of the lignocellulose itself.

Reverting, however, to the non-lignified fibres such as China grass, or Ramie (Böhmeria species), and the 'nettle fibres' generally, hemp, and even raw cotton—these all contain pectic bodies associated with the cellulose, which are hydrolysed and dissolved by treatment with boiling alkalis. But these pecto-celluloses have not been sufficiently investigated *as* compound celluloses to admit of any useful classification on the basis of particular constitutional variations of their non-cellulose constituents.

The mono-cotyledonous fibre-aggregates, whether fibre-vascular bundles (Phormium, Aloe fibres, Musa, etc.) or entire plants (Esparto, Bamboo stems, Sugar Cane), are largely made up of pecto-celluloses, with a greater or less proportion of lignocelluloses. But the constitution of these non-cellulose constituents is as yet quite unknown, and we have therefore none but the general basis of classification.

In the same way also the parenchymatous tissue of fruits, fleshy roots, etc.—the typical pecto-celluloses—must be, for the present, dismissed with the bare mention.

The investigation of these substances belongs rather to the province of general carbohydrate chemistry than to the narrower cellulose group; and the problems involved are in many respects rather morphological and physiological than purely chemical.

These same considerations apply also in great measure to the mucilaginous constituents of plant tissues, though certain of these have been investigated by modern chemical methods. The relationship of these substances to cellulose is indicated (*a*) by the histology of the tissues, which shows them to be associated with the *cell wall* rather than with the cell contents; (*b*) by their empirical composition, which is approximately that of

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cellulose; (*c*) by their reactions with iodine, by which they are coloured variously from blue to violet, as are the hydrated modifications of cellulose.* Beyond superficial observations of reactions (iodine) and gelatinisation with water, these compound celluloses—which may conveniently be termed muco-celluloses—had been but little investigated † until the systematic work of Kirchner and Tollens, and Gans and Tollens, ‡ upon the mucilages and gums.

Cuto-celluloses [*Adipo-celluloses*].—The plant represents, in the one view, an assemblage of synthetical operations carried on within a space enclosed and protected from the destructive influences of water and unlimited atmospheric oxygen. The protecting external tissues are those which we are about to describe as constituting the third important group of compound celluloses. These tissues contain, in admixture with the tissue-substance, a variety of oily and waxy products (easily removed by mechanical solvents), the presence of which adds very considerably to the water-resisting property of the tissue. It will be seen as we proceed, however, that the tissue-substance, after being entirely freed from these adventitious constituents or oily excreta, yields a large additional quantity of such products when decomposed by 'artificial' processes of oxidation and saponification. By this and by its empirical composition (*infra*) the tissue-substance will be seen to contain 'residues' of high carbon percentage and molecular weight, and closely allied in chemical structure to the oil and wax compounds found in the 'free' state in the tissue as it occurs in the plant. These groups are associated in combination in the tissue with cellulose residues, and hence the description of such complexes as adipo-celluloses.

There are two main types of these compound-celluloses, viz. cork and the cuticular tissues of leaves, stems, etc.

Cork in its ordinary form is a complex mixture containing not only oils and waxes, but tannins, lignocelluloses, and nitrogenous residues. The following are the results of elementary

* Sachsse, Farbstoffe, etc., p. 161. † Sachsse, *loc. cit.*
‡ Annalen, **175**, 205; **249**, 245.

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analysis: (*a*) of cork purified by exhaustive treatment with ether, alcohol and water; (*b*) of cork (*Quercus suber*) without purification; (*c*) of the cork tissue of the cuticle of the potato (tuber) purified by exhaustion with alcohol:—

	(*a*)	(*b*)	(*c*)
C	67·8	65·7	62·3
H	8·7	8·3	7·1
O	21·2	24·5	27·6
N	2·3	1·5	3·0

The analyses are calculated on the ash-free substance.*

These investigators succeeded in isolating cellulose from cork, but by complicated and drastic methods of treatment, such as would break down the greater proportion of the cellulose into soluble derivatives. These treatments were: (1) oxidation with nitric acid; (2) alternate treatments with boiling dilute hydrochloric acid and 10 p.ct. solution of potassium hydrate. The proportion thus isolated amounted to 2–3 p.ct. only.

The authors, on the other hand, have observed that the non-cellulose of cork is entirely converted into soluble derivatives by the process of digestion at high temperatures with solutions of the alkaline sulphites, as described, p. 68. In this way a residue is obtained preserving the form (i.e. cellular structure) of the original cork, and amounting to 9–12 p.ct.

The details of a particular experiment were as follows: 10·995 grms. cork, 20 grms. $Na_2SO_3.7H_2O$, 2 grms. Na_2CO_3, dissolved in 500 c.c. water. Digested three hours at 75 lbs., and four hours at 125 lbs. pressure. Residue bleached with sodium hypochlorite solution. Yield of cellulose, 1·34 grms.; 12·1 p.ct.

These relationships have been more definitely made out by Frémy, in his investigations of the closely allied compound which constitutes the epidermal or cuticular tissue of the leaves, stems, etc., of Phanerogams. As the characteristic constituent of cork is termed suberin, so Frémy terms this cuticular tissue-substance cutin or cutose. To prepare this substance, cuticular tissue ('peel') of the apple, e.g. is treated with boiling dilute

* Döpping, Annalen, **45**, 216; Mitscherlich, Annalen, **75**, 305.

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acids, followed by digestion with the cuprammonium reagent (p. 9); then again with boiling acid and dilute alkali (KOH); finally the residue is treated with alcohol and ether. In this way a nitrogen-free residue is obtained having the empirical composition :—

C	73·66 p.ct.
H	11·37 „
O	14·97 „

Not only by these results, but by the study of the proximate resolutions of this substance, it is shown to have the closest relationships to the carbon compounds of the 'wax' class.*

In a later investigation of the products of saponification of this substance, Frémy worked upon a raw material similarly prepared, but having the composition C 68·3, H 8·9, O 22·8. This compound is termed *cutose*, in substitution for cutin. Cutose is slowly attacked by boiling alkaline solutions; a product is dissolved, *of the same empirical composition* as cutose,† but of a fatty nature. It is precipitated on acidifying the solution; the precipitate is soluble in ether-alcohol, and when isolated is found to melt below 100°. Under more drastic treatment with alkaline solutions the dissolved products are found to be a mixture. Precipitated by acids and treated with boiling alcohol, the mixture dissolves: on cooling, the solution deposits an acid (m.p. 85°) in yellow-coloured flocks, which after fusion form a brownish translucent friable mass. This is a compound of *stearocutic acid* and *oleocutic acid* (*infra*), into which it is resolved by further treatment with alkali. The alcoholic filtrate from the solid acid when evaporated gives a viscous residue of an acid body, *oleocutic acid*.

By the further action of very concentrated potash solution on the yellow acid, stearocutic acid is formed. The potash salt of this acid is white and translucent, insoluble in water and cold alcohol, soluble in boiling alcohol. The free acid (m.p. 76°) is also insoluble in cold alcohol, slightly only on boiling, but dissolves in benzene and in acetic acid on warming. The acid also dissolves freely in alcohol in presence of oleocutic acid. A

* Compt. Rend, **48**, 667. † Comp. Lignocelluloses, p. 60.

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similar result is seen with the potassium salt, which, though insoluble in water, dissolves in an aqueous solution of potassium oleocutate.

The composition of these two acids is as under :—

Stearocutic Acid.

C	75·00
H	10·71
O	14·28

which is expressed by the formula $C_{28}H_{48}O_4$. This formula is confirmed by the analysis of the salts of the acid.

Oleocutic Acid.

C	66·66
H	7·91
O	25·43

expressed by the formula $C_{14}H_{20}O_4$.

Cutose is regarded by Frémy as a complex of these two compounds, in the proportion of 1 mol. stearocutic acid : 5 mols. oleocutic acid. These acids undergo alteration on heating at 100° in presence of water, passing into the insoluble modifications of higher melting point. The original molecular condition, however, is restored on heating with alkaline solutions.

Frémy also made observations upon suberin (or suberose), which yielded similar products of saponification. He therefore concluded that the two products are substantially identical. The products of oxidation by nitric acid are also indistinguishable, viz. chiefly suberic and succinic acids.

These results suggest, from the purely chemical standpoint, that the cellulose of the tissue and the waxy products of excretion stand to one another in a genetic relationship, and the cutose or suberose occupies an intermediate position. The question of a direct conversion of cellulose into wax taking place in these cuticular tissues was definitely raised and discussed by De Bary in his investigations of this group of plant constituents.* It appears from these researches that wax-alcohols are certainly not contained in the cell-sap or protoplasm, and

* Bot. Ztg. 1871.

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that their origin must be in the cuticular tissues themselves; but the parent substance may be either cellulose, or some compound built up with it in the ordinary course of elaboration. This question is left for the present undetermined. It should be borne in mind, on the other hand, that we have a great number of direct observations upon the physiological equivalence of the carbohydrates and the fats, both in the animal and vegetable worlds; and although the mechanism of the transformation of the one into the other group of compounds remains unelucidated, it is after all not more difficult to imagine than the condensation to furfural. It is, however, not the purpose of this treatise to carry discussion into purely speculative regions; and it is sufficient to state the conclusion that there is ample ground for adopting as a working hypothesis that carbohydrates, or possibly cellulose, are transformed into cutose or suberose, and these, again, into free waxy bodies of lower molecular weight, the whole process representing the change known as cuticularisation or suberisation.

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CHAPTER II.

PHYSICAL STRUCTURE OF FIBRES.

We now have to treat of the fibrous raw materials from the point of view of form or structure, which is, of course, a very important factor in determining the quality of the paper or other fabric into which they are manufactured. It is sufficiently evident that the strength of paper is primarily due to the cohesion of its constituent fibres. When paper is torn, the edges present a fibrous appearance, and observation teaches us that, other things being equal, the greater the manifestation of fibrous structure, the stronger will be the paper. If a paper be thoroughly wetted, its tensile strength is reduced to a minimum, and if subjected to a slight strain we get, not a tearing, but a pulling asunder of the fibres. If this be performed under a lens, the structure of the paper is more clearly seen, and it will be appreciated to what extent the qualities of a paper are the aggregate of the qualities of its constituent fibres. A more careful dissection of the papers shows that these fibres, which are *ultimate fibres*, as distinguished from the bundles of these, or *filaments*, which the spinner frequently employs, are interlaced in all directions. To produce this effect of interweaving, and to insure that uniformity which is an essential feature of good paper, we have among others the following contributory causes: (1) the deposition of the fibres from suspension in water; (2) the composition of the pulp with regard to the reduction of the fibrous bundles, and the isolation of the individual fibres; and (3) the *structure* of these ultimate fibres. It is with the last that we are chiefly concerned at present.

To convey a general notion of the influence of the structure

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of fibres upon fabrics, we shall with advantage travel outside our immediate province to consider briefly the woollen and silk manufactures in relation to this point. Wool is, as we know, a discontinuous fibre, and its structure is that represented in Fig. 1, the most conspicuous feature being its broken surface, consisting apparently of imbricated scales.

FIG. 1.

The silk fibre, on the other hand, is a dual cylinder, spun by the worm in a continuous length, and with a perfectly smooth surface. Now it would not be to our purpose to point out that, in starting from a discontinuous simple fibre to produce a continuous (therefore necessarily compound) one, a very different treatment or process of spinning is required from that which the opposite condition renders practicable. We will rather consider the influence of structure upon materials manufactured from these fibres. It is obvious that the wool fibres, brought into contact with one another, tend to interlock; whereas silk fibres if rubbed or pressed together, simply slide over one another, the result in the woollen fabric is, by multiplication of the effect, a shrinking or contracting in length and breadth. This interaction of fibres, and the phenomena to which it gives rise, is known as the *felting* of wool and woollen goods; this tendency, for the contrary reason, is not seen in silk fabrics. The production of paper from a disintegrated fibrous mass or pulp introduces similar considerations. That paper will be the stronger in which the constituent fibres are the better 'felted,' and the degree in which felting takes place will depend to a great extent upon the form or microscopic peculiarities of the fibres. This is only one of the more obvious inferences to be drawn from the structure of the fibres to the qualities of the papers which they compose. Other equally important practical bearings will be seen to attach to the microscopic study of our fibrous raw materials, and to

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the consideration of this branch of the subject we now ask the careful attention of the student.

Microscopical Examination.—Under the head of 'Microscopic Features' we must include everything which has to do with the structure of the vegetable fibres, as well as their organisation and distribution in the plant. In the analysis of 'organised' structures we employ the two methods (1) of *dissection*; (2) *examination* by means of the microscope; in other words, we first isolate the part under investigation by a mechanical process, and then proceed to the optical resolution or analysis of the part. Having by analysis acquired a knowledge of the *parts*, we study their mutual relations in the structure they compose—we integrate our knowledge, so to speak—by means of sections of the structure, cut so as to preserve the cohesion of the parts in section, and yet in so fine a film as to appear under the microscope to be virtually a plane surface. These points are illustrated in the drawings given.

It is impossible for us to deal specially with the subject of the microscope and its manipulation. The microscope, as a revealer of natural wonders, is one thing; as an instrument of scientific investigation, quite another. For the latter, the student must train himself by systematic work, and should especially concentrate his attention upon some *one* branch of natural history, however restricted.

We shall assume, in our treatment of the subject, a knowledge of the microscope as an instrument of research, such as can be easily acquired in a few weeks of work under the guidance of a teacher or of one of the excellent manuals which now abound.* We also assume a certain acquaintance with the elements of vegetable physiology, which it will be seen is necessary for a full grasp of the subject. Such an acquaintance, also, may be easily acquired, under direction, in a few weeks of work.†

We have before alluded to the difference presented by mono- and di-cotyledonous stems in regard to the distribution of their fibrous constituents. In illustration of this, we may cite Figs.

* 'Modern Microscopy.'—Cross and Martin J. Cole.

† 'Elementary Botany.'—Oliver.

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2, 3, which represent (2) a section of the aloe, (3) a section of the jute plant. The available fibres are in (2) the fibro-vascular

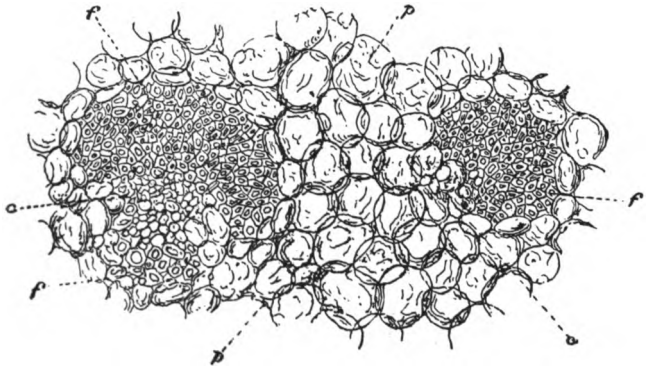

FIG. 2.

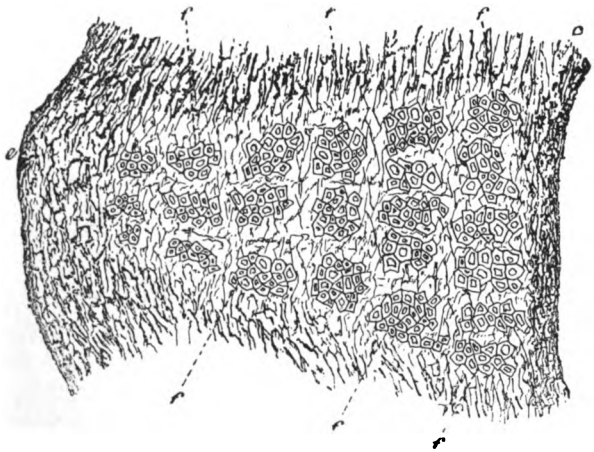

FIG. 3.

bundles (*f*), which are irregularly distributed throughout the main mass of cellular tissue, and in (3) the bast fibres (*f*), which constitute a definite and separate tissue. We have already

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alluded to the practical consequences of this typical difference of distribution, in regard to processes of separating these fibres on the large scale.

This process we have explained is necessarily simpler in the case of a fibrous *tissue*, definitely localised ; and this may be demonstrated by a superficial examination of a young branch of an exogen. As we know, the bark tissues are easily stripped from the underlying wood. If now we work up the former in a mortar, with a little water, we soon perceive the separation of the compound tissue into cellular matter, on the one hand, and *fibres*, the latter being more or less long and silky, according to

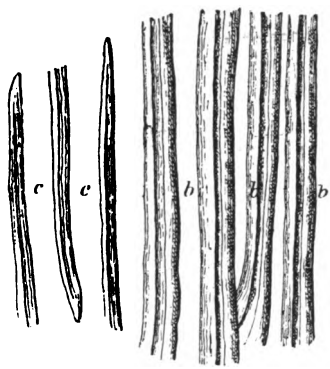

FIG. 4.

the plant from which they were isolated. They vary in length from one millimetre to several centimetres, and are aggregated together in the plant in such a way as to constitute bundles, often of very considerable length ; the general arrangement being comparable with that of the tiles in the roof of a house. It is important to distinguish the fibre-bundles from the elementary or normal *fibres*, and to this end they are designated by the term *filament*. Bast *fibres* are flexible and fusiform, terminating gradually in a point at either end, as represented in Fig. 4 ; bast *filaments*, built up of these fibres, containing often as many as twelve in the bundle, are usually cylindrical, but ex-

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hibit the widest differences in regard to the aggregation in degree as well as number and dimensions of their constituents. It is obvious that while the spinner has to do with these *filaments*, the paper-maker works up the ultimate fibre constituents or *fibres*. It is also an obvious corollary from this distinction that a fibrous material which from 'weakness' is unavailable for textile application, may yet be perfectly 'strong' from the paper-maker's point of view; in other words, the individual fibres may be strong, but have little cohesion in the filaments. As we proceed, the student will see more and more the practical bearings of this branch of the study, and will perceive the inferences to be drawn from the investigation of minute relationships to manufacturing processes and their products.

We shall say but little as to the necessary equipment. (1) A dissecting microscope, for dissecting under a lens, magnifying the object to 40 or 50 diameters. (2) an ordinary student's microscope, with lenses for magnifying to 100 and 300 diameters. This is adequate to the work, though, of course, it may be an advantage in certain cases to be provided with higher powers. (3) A glass slide, carrying an engraved scale of centimetres and millimetres for measuring the lengths of objects, and a micrometer, divided into $\frac{1}{10}$mm. for measuring diameters. It is also important to be able to determine the degree of enlargement under any particular combination of lenses, and for this purpose to possess a micrometer eye-piece, with a millimetre scale divided into hundredths. (4) An effective microtome, and the usual mounting accessories.

A very important feature in the diagnosis of fibres, more especially in regard to the composition of the fibre-substances, is the effect produced by treatment with various reagents. Certain of these reactions we have already indicated. We shall now give the details of composition of the several solutions which will be required.

Mounting Solutions.—In preparing objects for observation under the microscope, they may be mounted in water, or mixtures of glycerin with water. In examining fibres or fibrous structures under chemical treatment, they may be mounted

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in the solutions in which they are undergoing treatment. In mounting transparent objects it is sometimes required to employ a solution of the same refractive power as the substance itself. For this purpose, pure or diluted glycerin or a syrupy solution of calcium chloride may be employed; it is expedient to mix with either reagent a small proportion of acetic acid. When the objects are to be stained or otherwise treated while under observation, they must be first mounted in a neutral medium, e.g. water or dilute glycerin. The designation 'neutral' has reference to the fact that these reagents are without sensible action on the fibres.

IODINE SOLUTION.—We have previously described the preparation of a solution giving the characteristic blue reaction with cellulose directly. It is, however, often preferable to bring about this colouration in another way, and the following are the solutions employed: 1 gramme of potassium iodide is dissolved in 100 c.c. water, and the solution is saturated with iodine; it is preserved in stoppered bottles, containing a few fragments of the element, so as to keep up the saturation of the solution.

The accessory solution, dilute sulphuric acid, which is employed to determine the reaction between the cellulose and the iodine, is prepared as follows:—2 volumes of concentrated glycerin are mixed with 1 volume water, and to the mixture an equal volume of oil of vitriol (1·78 sp. gr.), is slowly added so as to prevent as far as possible a rise of temperature. The effect of the glycerin is very remarkable in preventing the distortion of the objects under the action of the acid, which in other respects remains uninfluenced.

By way of verification of this iodine test, which is somewhat capricious, it is advisable to test the reagents with a standard substance. The best for the purpose is a linen yarn which has been *partially* bleached. Under the action of the reagents the fibres composing this yarn (which must, of course, be suitably 'teased out' for mounting) are coloured a light blue, the centre, however, showing a yellow line, marking the distribution in the interior canal of a non-cellulose fibre constituent.

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Should these effects not appear, it may be concluded that the acid requires to be strengthened. On the other hand, too great a concentration is equally to be avoided; it is evidenced by causing a *distortion* of the fibre, easily recognised by comparison with the fibre mounted in a neutral medium.

CHLORINE WATER.—One of the most characteristic reactions of lignose, or lignified cellulose, is that of combining with chlorine. The reaction of the chlorinated derivatives with sodium sulphite solution is an important feature in the microscopic diagnosis of lignified fibres and cells. The reagent is prepared by dissolving chlorine to saturation in water. The sodium sulphite solution is prepared by dissolving the crystallised salt in 20 parts distilled water.

ANILINE SULPHATE SOLUTION.—With this reagent lignose gives a characteristic deep yellow colouration. A convenient strength is a 2 p.ct. solution of the salt. The colour is more quickly developed if the reagent is acidified; a few drops of sulphuric acid should therefore be added.

PHLOROGLUCOL REAGENT.—The crystalline phenol is dissolved to saturation in the cold in hydrochloric acid of 1·06 sp. gr. Lignified fibres and cells are stained a full magenta red by the reagent.

DIMETHYL-PARAPHENYLENE DIAMINE.—Solutions of this base are unstable, but the addition of acetic acid confers a more permanent character. The deep red colouration produced with the ligno-celluloses is useful in micro-chemical investigations.

SOLUTIONS OF COAL TAR COLOURS.—Some of these are of importance in enabling the microscopist to differentiate plant tissues. The 'affinities' of the fibre-substances for these are very various in kind and intensity. The phenomena of staining cannot be adequately treated in our histological scheme, which is necessarily very restricted. We therefore merely mention the more important colours which are used in staining, viz. magenta, methylene blue, malachite green, eosine, diphenylamine blue. A convenient strength is a solution of 1 in 2000. (See also p. 227.)

FERRIC FERRICYANIDE.—The red solution resulting from

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mixture of solution of a ferric salt and potassium ferricyanide, strikes a deep blue with the lignocelluloses and other tissue constituents containing unsaturated and oxidisible groups, and is a valuable aid in histological work. (See pp. 57 and 96.)

The above-mentioned reagents are a sufficient equipment for all ordinary work. Their employment presents no difficulties, and therefore no detailed descriptions are necessary. In more advanced investigations, the student will make his own selection of special reagents according also to the composition of the colouring matter. In following up this subject, he will require to consult works on vegetable histology.

Preparation of the Objects.—The necessary preliminary to the examination of the fibres themselves is their isolation. This is accomplished either by means of the dissecting microscope, or more roughly, according to circumstances. Having obtained the filaments, they are boiled in a 10 p.ct. solution of sodium carbonate, or a 2 p.ct. solution of caustic soda (NaOH), until sufficiently softened to yield easily to the 'teasing' needles. In certain cases the boiling must be supplemented by trituration in a mortar; this, or some similar operation, is especially necessary when the fibres are embedded in a mass of cellular tissue (parenchyma), e.g. in the fibro-vascular bundles of monocotyledons.

Sections of the filaments are prepared by cutting in a microtome, the filaments being previously agglutinated into a stiff bundle by means of any of the usual stiffening solutions, and, after drying, embedded in wax in the usual way. Sections of fresh stems and tissues are cut with a 'section' razor.

As an agglomerating agent, solutions of the cellulose sulphocarbonate, containing 2–3 p.ct. of dissolved cellulose, are especially to be recommended. In place of wax, a strong alcoholic solution of ordinary yellow soap is used with advantage as a medium for embedding. The specimens are introduced into the hot solution, which sets on cooling to a firm sectile mass.

Having prepared the objects, their examination under the microscope necessarily divides itself into (1) the determination of external features; (2) the diagnosis of chemical composition.

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The fibres themselves will be individually considered in regard to microscopic features.

There is one aspect of these structural features, however, which admits of more general treatment, and in respect of which we may anticipate with advantage, viz. the dimensions or simple elements of form. The importance of the determination of the length and diameter of both filaments and fibres will be readily appreciated by an inspection of the following table, in which the numbers are given for several of the more important.

TABLE OF LENGTHS OF RAW FIBRES (FILAMENTS) AND DIMENSIONS OF CONSTITUENT CELLS AND FIBRES.

	—	Average Length of Filament.	Average Length of Fibres.	Diameter of Cells.	
				Extreme.	Normal.
		mm.	cm.	$\frac{1}{100}$ mm.	$\frac{1}{100}$ mm.
A. *Seed Hairs.* Filaments composed of individual cells.	Cottons. *Gossypium Barbadense* . . (Sea Island)	..	4·05	1·92–2·79	2·52
	Gossypium accuminatum .	..	2·84	2·01–2·99	2·94
	Gossypium arboreum . .	..	2·50	2·00–3·78	2·99
	Bombax heptaphyllum .	..	2–3	1·9–2·9	..
B. *Bast-fibres.* Filaments or fibre bundles, made up of individual fibre-cells aggregated together.	Flax. *Linum usitatissimum* . .	20–140	2·0–4·0	1·2–2·5	1·6
	Hemp. *Cannabis sativa* .	100–300	..	1·5–2·8	1·8
	China Grass. *Boehmeria nivea* . .	..	22·0	4·0–8·0	5·0
	Ramie. *Boehmeria tenacissima* . .	..	8·0	1·6	..
	Jute. *Corchorus capsularis* . .	150–300	0·2	1·0–2·0	1·6
	Corchorus olitorius	150–300	0·2	1·6–3·2	2·0
	Paper mulberry. *Broussonetia papyrifera*	..	0·7–2·1	..	3·6
	Linden bast. *Tilia grandifolia* . . .	..	1–1·6	..	1·5
C. Fibro-vascular bundles.			mm.		
	New Zealand Flax. *Phormium tenax* .	80–110	2·5–5·6	0·8–1·9	1·3
	Aloe. *Aloe perfoliata* .	40–50	1·3–3·7	1·5–2·4	..
	Esparto. *Stipa tenacissima*	10–40	0·5–1·9	0·9–1·5	..

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A careful study of this table in relation to the application of these several fibres, will show that the correlation of the latter with these ultimate dimensions is close and essential.

These measurements of length and diameter are made in various ways. Thus, the object may be made to move across the field of vision, the extent of movement being recorded by means of a vernier attached to the stage itself. Another device is that of the micrometer eye-piece, by which a graduated scale is brought into the field of vision and is brought to bear upon any object, just as an ordinary measuring rule or tape.

A very important point in the diagnosis of a raw material, and next in order of treatment, is the degree of purity of the substance, in so far as this is related to structure. The fibres may be associated with cellular tissue, or with cellular débris, if they have undergone the retting process or other treatment for separation; or with 'incrusting and intercellular substances'; in various proportions. In the latter case the association with the fibres is usually much more intimate; they are, in fact, essential constituents of the fibre *bundles* (lignified bast-fibres, fibro-vascular bundles), whereas the former we may regard as 'foreign matter.' We may, however, distinguish between the normal 'incrustation' of the fibre-cells, and such an incrustation of the filaments as would be described as a loose adhesion of non-fibrous matter. The latter is seen in such tissues as the bast of the adansonia, and the fibro-vascular bundles of the aloes. These are points with which observation alone can familiarise the student; as experience grows he will find it increasingly easy to follow *general* distinctions, and in proportion as he uses his own faculties, so he will be able to generalise for himself. He will find this equally true of the second section of the microscopic examination, i.e. the micro-chemical diagnosis of fibres. Under this head is included the observation of the behaviour of fibres towards the various reagents above described. In addition to their microscopical employment, it is useful to note their effect on fibres in the gross, both in their natural state and after treatment with bleaching agents.

In applying the iodine reaction, attention must be paid to

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the following details of manipulation. Place the object (dry) upon the glass slide, moisten with a few drops of the iodine solution, cover with a glass slip, and examine under the microscope. Note the effects, which are those of the iodine alone. Then remove the iodine solution by means of blotting paper, and introduce the sulphuric acid by the method of 'irrigation.' The colouration of the cellulose (blue-violet) is immediate; it has the effect, moreover, of bringing out more clearly a number of the structural details of the fibre.

We have already treated of the resolution of the raw fibres into cellulose and non-cellulose constituents by processes which convert the latter into soluble derivatives. The student will derive much instruction from following up the attendant structural disintegration with the aid of the microscope, especially if associated with reactions of ferric ferricyanide. The chemical dissection of lignified fibres by the alternate action of bromine-water and alkalis, should be studied by mounting specimens of the fibre at all stages, and carefully noting all the changes which occur. The more drastic action of chlorine should also be studied by mounting the chlorinated fibre (in water) and then irrigating with the alkaline solvent (caustic alkali or sulphite) and noting, the stages in the completion of the disintegration.

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CHAPTER III.

SCHEME FOR THE DIAGNOSIS AND CHEMICAL ANALYSIS OF PLANT SUBSTANCES.

It will be convenient at this point to present to the reader a general scheme for the chemical analysis of fibrous raw materials.

We have already described various methods for the determination of cellulose in fibrous substances. This is to the paper-maker the most important constituent, and is that upon which his calculations of the value of a raw material are based. Not only, however, is it of the greatest importance for him to be able accurately to determine the *amount* of cellulose, but it is necessary to be able to form some idea of the nature of the cellulose, and also the ease with which it can be obtained from the fibre. This latter point can only be properly established by direct trial of the fibre under the conditions existing in the factory. A practical assay of a raw material for 'paper-making cellulose' is best carried out in a model digester capable of treating from 500 to 1000 grammes of raw material. In such an apparatus a digestion with alkaline lye, or with bisulphite liquor can be carried out at elevated temperatures exactly as on the large scale.

Where such small digester is not available, the fibrous material may be inclosed in a bag of resistant material, sufficiently open to allow for penetration of liquid, and close enough to prevent escape of fibre. The bag is placed in the ordinary boilers in the mill, as charged with material for 'boiling'; at the conclusion of the 'boil' it is removed to the laboratory and worked up by washing, etc., for the complete isolation of the fibre.

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To complete the purification of the cellulose, where this is necessary, it is bleached with a solution of bleaching powder. The experiment is made a quantitative measure of the amount of bleaching chlorine required, by taking a measured volume of a solution of known strength, in calculated excess, and, when the bleaching of the fibre is completed, estimating the 'residual chlorine' by an observation in a known fraction of the liquid with which the bleached pulp is in contact.

In the manipulation of fibrous materials, filters of cotton cloth will be found useful. The qualities most suitable are the ordinary printers' calico (bleached), nainsook, and muslins of varying fineness according to the nature of the material. These filters may be supported in glass funnels, and, after collecting and washing the fibrous product, the mass may be tightly squeezed to retain not more than its own weight of water. After squeezing, it is easily detached from the cloth.

Filters of wire cloth, such as paper machine wire, suitably mounted, are particularly useful. Regard must be paid to the dimensions of the mesh in all cases.

By the operations of isolating the cellulose, preceded or accompanied by microscopic observations such as we have described, a fair general account will have been given of any fibrous material. But, to complete the investigation, a scheme of determinations should be carried out as shown on the next page.

These determinations are the practical application of the principles elucidated in Chapter I. It only remains now, therefore, to add certain notes of practical points to be observed in the experimental study of raw materials.

1. (*a*) MOISTURE.—The mere operation of drying at 100° determines molecular changes in such compounds as the lignocelluloses—changes which affect the subsequent action of reagents. It is necessary, therefore, to weigh separate portions for the particular experiments in the air-dry condition, and calculate the dry contents from the data of the specimen weighed after drying at 100°.

(*b*) FAT, WAX, AND RESIN. — These constituents are

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estimated as an aggregate extract obtained by boiling out with hydrocarbon solvents, or with ether-alcohol, using the portion previously dried for 1 (*a*).

Separate portion taken for each determination. Results calculated in percentage of dry substance.	Moisture . .	Hygroscopic water, or water of condition. Loss in drying at 100°.
	Fat, Wax and Resin	By extraction with solvents.
	Ash . . .	Total residue left on ignition.
	Hydrolysis (*a*) .	Loss of weight on boiling 5 minutes in 1 p.ct. solution of caustic soda.
	,, (*b*) .	Loss of weight on continuing to boil 1 hour.
	Cellulose . .	Isolation and estimation as previously described.
	Mercerising . .	Loss of weight on treating 1 hour with strong solution of caustic soda, 15–25 p.ct. NaOH.
	Nitration . .	Weight of nitrated product obtained by treatment with mixture of equal volumes of nitric and sulphuric acids 1 hour in the cold.
	Acid purification .	Loss of weight after boiling with 20 p.ct. acetic acid and washing with water and alcohol.
	Carbon percentage	Determined by combustion.

2. ASH.—The specimen weighed after drying at 100° may then be burned for the determination of ash. The ash in isolated fibres is low, viz. 1–2 p.ct.; in fibre aggregates it is often high—thus, in esparto and straw, from 3–6 p.ct.—and should be taken into account in calculations of yields or loss of weight. In such cases, after weighing the product of any given reaction, the specimen, or a portion of it, should be burned and the ash determined. The ash-free product is calculated in terms of the original substance, also taken ash-free.

The ash constituents are (1) those of the normal fibre, and (2) in certain cases, adventitious mineral matter. These are easily distinguished and separately estimated.

3. ALKALINE HYDROLYSIS.—This is obviously the first stage towards the isolation of cellulose. When the numbers obtained for the short period (*a*) and for the long digestion (*b*)

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show a marked difference, it is an obvious general indication of low paper-making quality.

4. CELLULOSE.—Having isolated a white residue from a raw fibrous material, it may be weighed and then further investigated. An estimation of furfural will establish its position in the classification of the celluloses.* For practical purposes it is sufficient to establish the degree of resistance of the cellulose to further alkaline hydrolysis and to oxidation by alkaline cupric oxide (Fehling's solution).

5. MERCERISING.—The effect of the action of caustic soda as measured by loss of weight, and also changes in appearance and structure, may be usefully observed on the isolated celluloses, and in certain cases upon the raw fibrous materials. The pecto-celluloses are considerably gelatinised by the treatment, the fibres often undergoing agglomeration, and drying to a harsh wiry condition. The ligno-celluloses are affected in the contrary direction. The cuto-celluloses are not all attacked. From all the above treatments the product should be treated with dilute acids by immersion in the cold, and copiously washed before drying. The drying is much accelerated by treatment with alcohol.

6. 'NITRATION,' or conversion into nitric esters, affords useful information; but judgment must be exercised as to the applicability of the treatment to the raw material, to the partially purified products (alkaline hydrolysis), or to the isolated cellulose. It is a general measure of the proportion of reactive alcoholic OH groups, and also of resistance to oxidation.

7. ACID PURIFICATION removes basic mineral matter, often present in some quantity in raw materials of the pecto-cellulose class. It may sometimes be required to attack and remove more resistant mineral constituents such as silica and silicates. In this case the material may be digested with a mixture of hydrofluoric and hydrochloric acids in vessels suitably resistant to the action of these acids. The treatment is followed by copious washing.

8. CARBON PERCENTAGE.—This is only necessary in certain

* For which, see *ante*, p. 48.

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investigations. The value of the constant will be recognised from the fact that it varies considerably for the different groups of compound celluloses. The most convenient method is that of combustion with chromic acid after solution in sulphuric acid.*

In addition to the above, other determinations may in certain cases be usefully carried out. Thus an observation of the loss of weight in boiling with dilute acid (1 p.ct. HCl, or H_2SO_4) supplies an approximate measure of the more easily hydrolysed carbohydrates, e.g. hemi-celluloses. The ferric ferricyanide reaction especially characteristic of the ligno-celluloses, may be quantitatively carried out, the fibre being prepared by a weak alkaline treatment, washed and placed in a cold solution of the reagent at standard strength, prepared by mixing equal volumes of solutions of ferric chloride containing 16·2 grms. $FeCl_3$ per litre, and of potassium ferricyanide containing 33 grms. K_3FeCy_6 per litre. The gain in weight due to the deposit of the Prussian blue is a measure of the lignone groups.†

Investigations of the more extended character will be found indispensable in the examination of raw materials which are 'new,' or as yet untried as sources of paper-making fibres. But for what we may call standard materials, it is obvious that the practically important characteristics are those which relate to cellulose—quantity and quality—and the degree of resistance of the cellulose to alkaline hydrolysis and oxidation.

* The details of the method will be found described in Journ. Chem. Soc. **53**, 889.

† See 'Cellulose,' p. 124; and H. C. Sherman, Journ. Amer. Chem. Soc. 1897, **19**, 291-310.

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CHAPTER IV.

AN ACCOUNT OF THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE PRINCIPAL RAW MATERIALS.

THIS chapter contains the results obtained from an investigation of the different plant fibres by the methods indicated in the two previous chapters.

In the following table the fibres are classified according to the reactions which they give with iodine solution.

CLASSIFICATION OF PLANT FIBRES ACCORDING TO THEIR COLOUR REACTION WITH IODINE SOLUTION (VÉTILLART).

	A Seed Hairs.	B. Dicotyledonous Bast Fibres.	C. Monocotyledonous Fibres.
Blue reaction	Cotton.	Linen. Hemp. China grass. Paper mulberry. Sunn.	Straw. Esparto. Pine apple.
Yellow reaction		Jute. Hibiscus.	New Zealand flax. Yucca. Aloe. Manila hemp.

CLASS A.

Cotton.—Genus *Gossypium*. Order *Malvaceæ*. Seed hairs, consisting of ultimate fibres. Length, 2·0–4·0 cm., diameter, 0·012–0·037 mm. Mean ratio, 1250. Illustrated in Fig. 5: *a*, sections; *b*, longitudinal views; *c*, ends; mag. 300.

Microscopic features.—Fibre simple, opaque, flattened, always more or less twisted upon itself, side wall membranous, showing striæ.

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Sections—Simple, oval, irregular, central cavity often containing granules.

Micro-chemical reaction—Blue with iodine solution.

General chemical characteristic.—Pure cellulose basis with slight admixture of colouring matters, etc.

COMPOSITION OF RAW FIBRE.

	Church.	Müller.
Cellulose	91·15	91·35
Fat	0·51	0·40
Aqueous extract (containing nitrogenous substances)	0·67	0·50
Water	7·56	7·00
Ash	0·11	0·12
Cuticular substance (by difference)	..	0·63

E. Schunck, in his investigation of cotton bleaching,* finds that in boiling with sodium carbonate solution the fibre loses 5 p.ct. in weight. Some portion of the dissolved substances

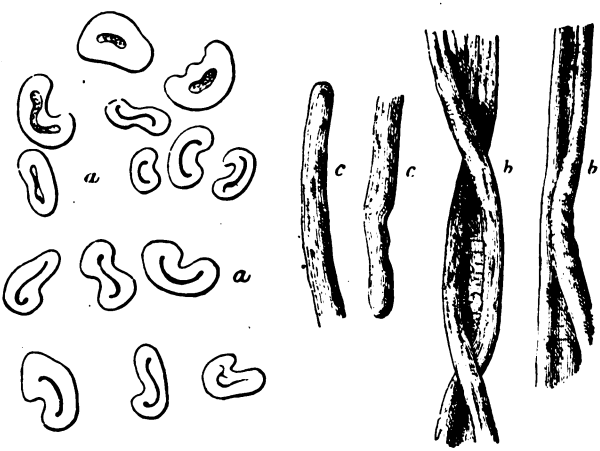

FIG. 5.

is precipitated on acidfying, and is found to contain a wax, resinous and brown colouring matters, and pectic acid.

Forms in which employed: Fibrous refuse from the decortication of the seeds; spinning waste, threads, rags, new and old.

* Chem. News, 17, 11.

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Class B.

Flax.—Genus *Linum*. Order *Linaceæ*. Bast-fibre and filaments. Lengths of fibres, 25–30 mm.; diameter, 0·02 mm., ratio, 1200. Illustrated in Fig. 6 : *a*, sections of the fibres, isolated and in groups ; *b*, the fibres viewed longitudinally, one

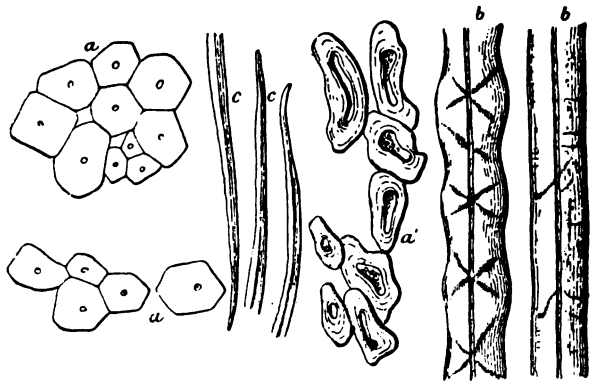

Fig. 6.

showing the creases produced by repeated bending ; *c*, ends ; *a'*, sections of fibres situated near the butt of the plant ; mag. 300.

Microscopic features.—Fibres transparent, regular, with tapered ends, side walls thick, consequently central canal small, smooth externally, sometimes slightly striated. Filaments easily split up into fibres.

Sections.—Polygonal, regular, angles more or less acute, lumen represented by point ; slight indications of concentric arrangement of fibre-substance.

Micro-chemical reaction.—Blue with iodine solution.

General chemical characteristic.—Pecto-cellulose with residues of wood (ligno-cellulose) and cuticle (cuto-cellulose).

Composition of raw fibre.—This varies with the different species, and is doubtless also influenced by variations in the

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processes of retting. The following are the analyses of two samples of Belgian flax (heckled) :—

	Müller.	
Cellulose	81·99	70·75
Fat and wax	2·37	2·34
Aqueous extract	3·62	5·94
Pectous substances	2·72	9·29
Water	8·60	10·56
Ash	0·70	1·32

The chemistry of the flax fibre has been investigated by Kolb, F. Hodges, and the authors.*

Forms in which employed.—Scutching refuse, spinning waste, threads, rags, new and old.

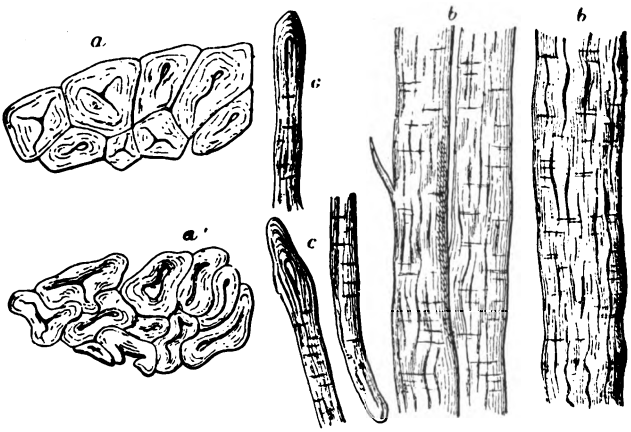

FIG. 7.

Hemp.—*Cannabis sativa.* Order *Cannabinaceæ.* Bast-fibres: length, 22 mm.; diameter, 0·022 mm.; ratio, 1000. Illustrated in Fig. 7: *a*, *a'*, sections of groups of fibres of the first and second zone respectively; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

Microscopic features.—Compact bundles. Fibres show striæ

* Journ. Chem. Soc., 1890, **57**, 196.

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and fissures, and often fibrillæ, detached or adherent. The central canal almost obliterated; ends of fibres large and flattened. The bundles show fine transverse markings.

Section.—Well marked concentric zones of fibre-substance, irregular in outline.

Micro-chemical reaction.—Blue and yellow reaction with iodine solution, the joint result showing green coloration.

General chemical characteristic.—Pecto-cellulose.

COMPOSITION OF RAW FIBRE (ITALIAN HEMP).

	Müller.
Cellulose	77·13
Fat and wax	0·55
Aqueous extract	3·45
Pectous substances	9·25
Water	8·80
Ash	0·82

Forms in which employed.—Scutching refuse, spinning waste, threads, cuttings, and rope ends.

Sunda or Sunn Hemp.—Genus *Crotalaria*. Order *Papilionaceæ*. Bast filaments: length 7–8 mm.; diameter, 0·03 mm.; ratio, 200.

Microscopic features.—Generally similar to those of hemp.

Micro-chemical reactions.—With iodine various, from blue to yellow. With aniline sulphate, slight yellow.

General chemical characteristics.—Pecto-cellulose (with some ligno-cellulose).

The following are the results of analysis of the raw fibre (H. Müller):

Cellulose	80·01
Fat and wax	0·55
Aqueous extract	2·82
Pectous substances	6·41
Water	9·60
Ash	0·61

This fibre, exported from India and the Sunda Islands, has found employment in Spain and Portugal, but up to the present has not been adopted to any extent in other parts of Europe.

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China Grass, Rhea, Ramie.—Genus *Böhmeria*. Order *Urticaceæ*. Bast filaments: length 120 mm.; diameter, 0·05 mm.; ratio, 2400. Illustrated in Fig. 8: *a*, section of a bundle of fibres; *b*, a fibre seen longitudinally; *c*, ends; mag. 300.

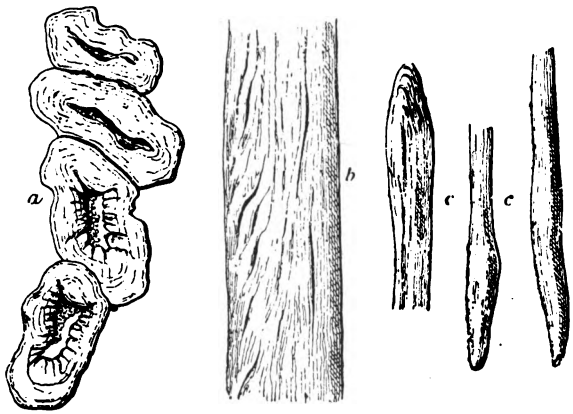

FIG. 8.

Microscopic characteristics.—Irregular in form and length; often conspicuous in respect of latter (see Table, p. 89); fibre sometimes cylindrical, either smooth or striated, sometimes flattened; central canal well developed, often containing granules; extremities of fibres rounded, spatulated, or lance-shaped. Sections marked by numerous concentric layers, often showing radiating striæ.

Micro-chemical reaction.—Blue to violet, with iodine solution.

General chemical characteristics.—Pecto-cellulose.

Composition of raw fibre (H. Müller):—

Cellulose	75·83	62·50
Fat and wax	0·20	0·56
Aqueous extract	6·29	9·76
Pectous substances	6·07	12·00
Water	8·74	9·55
Ash	2·87	5·63

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Forms in which employed.—This material has been the subject of successful experiments, which have resulted in a limited use of the fabric for papers of special character; imparts great tensile strength to paper. The portions available are as in flax.

Common Nettle.—*Urtica dioica.* Order *Urticaceæ.* Bast filaments: length 27 mm.; diameter, 0·05 mm.; ratio, 550.

Microscopic characteristics.—Similar to the above.

The fibres of this plant were, in the olden times, separated in the same way as flax, and worked up into cloth. At present it has no practical interest to the paper-maker, but deserves attention at the hand of the student, as the most easily accessible for the purpose of study. It is, moreover, possible that, under cultivation, it may yet become a source of raw material for paper-making.

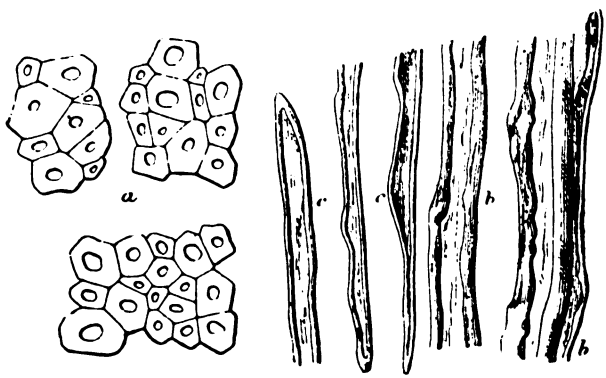

FIG. 9.

Jute.—*Corchorus.* Order *Tiliaceæ.* Bast: length, 2 mm.; diameter, 0·022; ratio, 90. Illustrated in Fig. 9: *a*, section of bundles of fibres; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

Microscopic features.—Compact bundles; fibres smooth.

Micro-chemical reactions.—Yellow-brown, with iodine;

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yellow, with aniline sulphate; bright yellow, with chlorine water: changed to carmine by treatment with sodium sulphite solution.

General chemical characteristic.—Ligno-cellulose. The chemistry of jute as the type of ligno-cellulose has been treated on pp. 56–64.

Composition of raw fibre (Müller):—

	1st quality.	Cuttings or Butts. (Root ends.)
Cellulose	63·76	60·89
Fat and wax	0·38	0·44
Aqueous extract	1·00	3·89
Non-cellulose, or lignone	24·32	20·98
Water	9·86	12·40
Ash	0·68	1·40

Forms in which employed.—Threads, "butts," bagging.

Bast Tissues.—We have alluded, in our opening remarks, to the broad division of the bast of exogens or dicotyledonous plants into coherent and non-coherent tissues. We have now considered the more important of the latter, and we find that they are obtained from the stems of annuals. We find also that while they constitute a tissue, in the sense of being definitely localised, the constituent fibres are disposed in parallel series of independent bundles or filaments, which are isolated by a mechanical operation after the whole stem has undergone the preparatory retting process. In exogens of longer and larger growth, the bast, as might be expected, becomes a coherent compound tissue, which is, in many cases, easily detached from the underlying wood. We shall mention three of these as receiving very important applications: though only one has been applied to any extent by the paper-makers of this country. This, which we shall consider first, is the bast of the *Adansonia digitata*, or baobab, a tree which flourishes in the tropical regions of the west coast of Africa. It is exported chiefly from Loanga, in the form of fibrous lumps of a brown colour. These are seen to be composed of a network of bast bundles, which are but slightly coloured, intersected by medullary rays of a dark brown colour. The microscopic features of the fibre are those which

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are generally characteristic of the bast of exogens: we do not know that we could cite any whereby it could be identified with certainty.

The fibres give a yellow colouration with aniline sulphate, but they contain only a small proportion of lignose. The following are the results of analyses of this bast:—

Cellulose	49·35	58·82 *
Fat and wax	0·94	0·41
Aqueous extract	13·57	7·08
Pectous substances	19·05	15·19
Water	10·90	13·18
Ash	6·19	4·72

* Made up of { 13·75 cellulose from medullary tissue. 45·07 cellulose of fibres.

Linden Bast (*Tilia Europæa*) is the raw material employed in the manufacture in Russia of the mats so largely used in this country, for wrapping furniture and heavy goods, and also by gardeners for a variety of purposes. One of the features of this bast is the strong cohesion of the fibres in the bundles or filaments. They are resolved, but with difficulty, on long boiling, with a solution of carbonate of soda, the soluble products being of a mucilaginous nature. This bast has not been applied to any extent by the paper-makers of this country.

Bast of the Paper Mulberry (*Broussonetia papyrifera*). This product deserves mention, not from its importance to the European paper-maker, but because of its application to the manufacture of the peculiar papers of the Chinese and Japanese. The special features of this, and the other basts which are similarly employed in these countries—*Edgworthia papyrifera*, *Broussonetia kaempferia*, are (1) the ease with which the coherent fibrous tissue is separated from the parenchymatous tissue which accompanies it: (2) its comparative freedom from medullary rays; (3) the great length and fineness of the fibres. These properties conduce to its ready conversion into a well felted paper, of great tensile strength, and remarkable softness.

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Class C.

The more important raw materials in this class are whole stems of monocotyledonous annuals. The isolation of fibres for paper-making from these plants depends upon a chemical process of resolution ; the pulp obtained is, therefore, a complex of the various orders of cell-fibres contained in the plant.

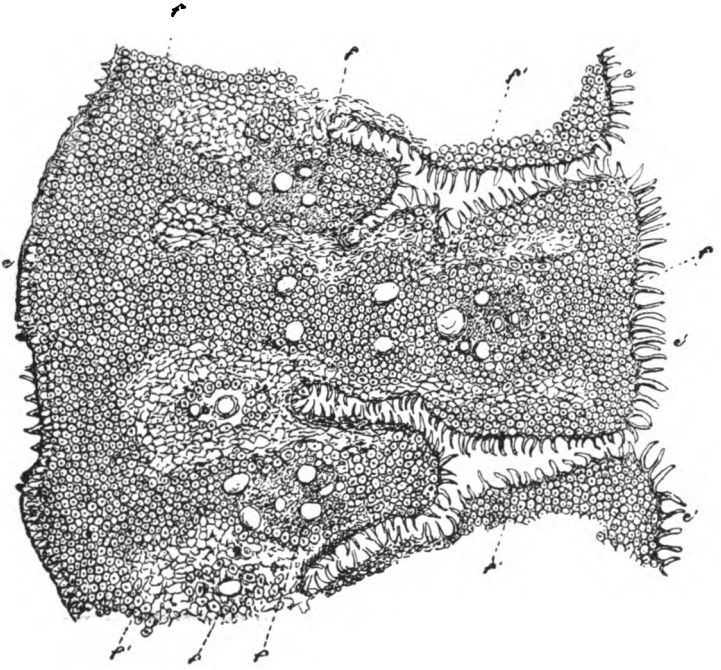

Fig. 10.

While the pulp consists for the most part of the vessels of the fibro-vascular bundles, it contains in addition the serrated cuticular cells which are so characteristic of this group. They therefore present a general similarity in microscopic features ; there are, however, certain individual characteristics, such as

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the form and dimensions of particular cells which serve for the identification of the various pulps. Where such occur they will be indicated.

Esparto.—*Stipa tenacissima* and *Lygeum Spartum*.

Order, *Gramineæ*. Bast fibres of fibro-vascular bundles and fibrous elements of the ground-tissue. Length, 1·5 mm.; diameter, 0·012 mm.; ratio, 125. Illustrated in Figs. 10, 11. In Fig. 10, the fibro-vascular bundles *f* are seen spread throughout the interior of the leaf, but the intervals, instead of being occupied by parenchyma, with large cells and thin walls, are filled with a compact mass of fine solid fibres *f'*; *e*, external epidermis; *e'*, internal epidermis; mag. 100. In Fig. 11, *a* is a

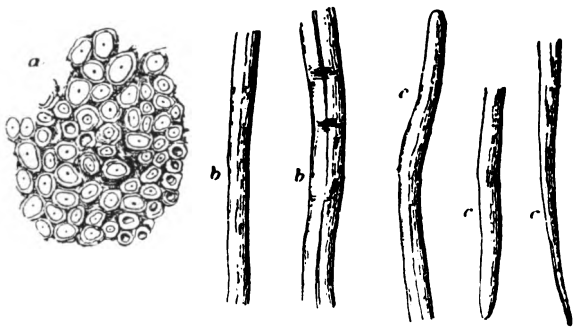

FIG. 11.

section of a group of fibres; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

Microscopic features.—Short, smooth, cylindrical, uniform in diameter, central canal very small, extremities rounded, truncated and bifurcated.

Section.—Minute, generally oval, sometimes polygonal; central cavity represented by a point.

Micro-chemical reaction.—Both blue and yellow with iodine solution.

In examining a paper containing esparto under the microscope, the pulp will be found to contain, in addition to the

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fibres of the fibro-vascular bundles, a certain number of the cuticular cells (see Fig. 12), together with some of the fine

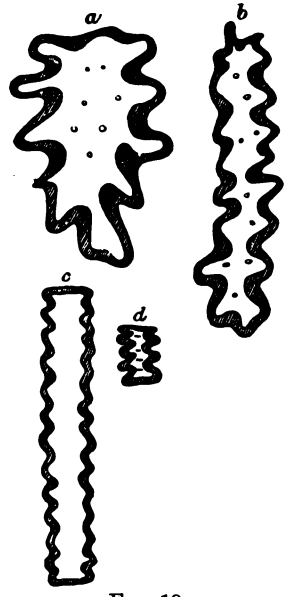

FIG. 12.

hairs which are seen in the section (Fig. 10). These are very characteristic.

General chemical characteristics.—Pecto-cellulose mixed with some ligno-cellulose.

Composition (Hugo Müller) :—

	Spanish.	African.
Cellulose	48·25	45·80
Fat and wax	2·07	2·62
Aqueous extract	10·19	9·81
Pectous substances, etc. . . .	26·39	29·30
Water	9·38	8·80
Ash	3·72	3·67

Straw.—Order, *Gramineæ*.

Microscopic features.—Generally similar to those of esparto. There are, however, differences of shape and dimensions of the

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serrated cuticular cells, which differentiate the various kinds of straw from each other and from esparto.

In Fig. 12 are shown these cells from maize-straw (*a* and *b*) from rye-straw (*c*), and from esparto (*d*). The following table gives the dimensions of the cells from different kinds of straw :—

	Length.	Breadth.
Barley . .	0·103–0·224 mm.	0·012–0·014 mm.
Rye . . .	0·086–0·345 „	0·012–0·016 „
Wheat . .	0·152–0·449 „	0·018–0·024 „
Oats . . .	0·186–0·448 „	0·012–0·017 „

Another distinctive feature of straw fibre is the presence in it of a number of oval cells, derived from the 'pithy' matter

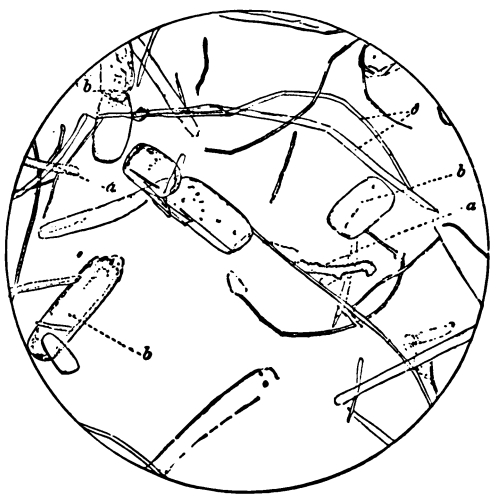

FIG. 13.

attached to the inside of the stem. These are clearly shown at *b* (Fig. 13), which represents the general appearance of straw pulp.

General chemical characteristics.—Both ligno-cellulose and pecto-cellulose.

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The following are the results of analyses of straws (Hugo Müller) :—

	Winter Wheat.	Winter Rye.
Cellulose	46·60	47·69
Fat and wax	1·49	1·93
Aqueous extract	8·07	0·05
Non-cellulose or lignin	28·49	26·75
Water	9·85	11·38
Ash	5·50	3·20

Bamboo and Sugar-Cane.—Order, *Gramineæ*.

From the close botanical relationship of these products to the stems of the Gramineæ of our own climate, their microscopic features are, as might be expected, similar to those of straw. The similarity is further shown by the chemical composition (Hugo Müller) :—

	Air-dried.
Cellulose	50·13
Fat and wax	0·78
Aqueous extract	10·56
Lignin and pectous substances	24·84
Water	8·56
Ash	5·13

New Zealand Flax.—*Phormium tenax*. Order, *Lineaceæ*. Fibro-vascular bundles of the leaves.

Microscopic characteristics.—Length of fibres 9 mm.; diameter, 0·016 mm.; ratio, 560. Fibres are fine, regular and smooth; the walls are uniform; central canal small; extremities vesicular. The fibres have little cohesion in the bundle. Sections.—Round or polygonal.

Micro-chemical reaction.—Yellow, with iodine solution. Characteristic deep red colouration with concentrated nitric acid (Müller).

General chemical characteristic.—Ligno-cellulose. It contains 86·3 per cent. of cellulose.

Manila Hemp.—*Musa textilis*, Abacá. Order, *Musaceæ*. Fibro-vascular bundles of leaves.

Microscopic characteristics.—Length of fibres, 6 mm.; diameter, 0·024 mm.; ratio, 250. Fibres, white, lustrous; the walls are uniform; central cavity large and very apparent. Fibres easily detached.

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Sections.—Round or polygonal. Illustrated in Fig. 14: *a*, section of bundle of fibres; *b*, fibres seen longitudinally; *c*, ends; mag. 300.

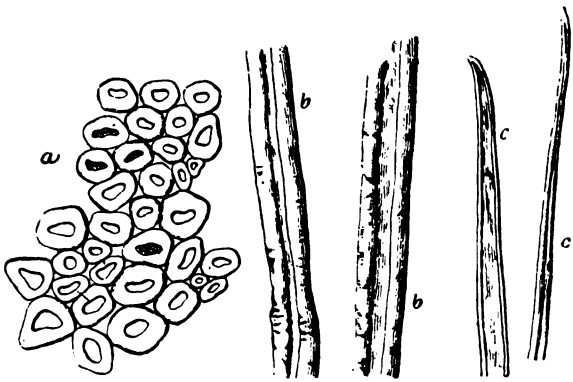

FIG. 14.

Micro-chemical reaction. — Yellow with iodine solution. Composition (Hugo Müller).

Cellulose	64·07
Fat and wax	0·62
Aqueous extract	0·96
Lignin and pectous substances	21·60
Water	11·73
Ash	1·02

Wood.—The greater portion of the 'chemical' wood pulp used in this country is prepared in Scandinavia and Canada, from trees belonging to the order *Coniferæ* (Gymnospermia) more particularly from the genera *Abies* and *Pinus*. In America especially, and on the Continent, pulps prepared from poplar and other dicotyledonous woods are largely employed, and increasing quantities are being imported for use in this country. The *Coniferæ* yield a larger proportion of cellulose (pulp) than most other woods; the ultimate fibres, moreover, are longer, and for these reasons this class of wood is generally

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preferred. On the other hand, poplar pulp has certain special paper-making qualities.

Micro-chemical reactions.—Thoroughly boiled chemical wood pulp is coloured blue by the iodine reagents.

The cellulose pulps of the coniferous woods consist almost entirely of fibrous elements (tracheids), the parenchyma cells of the medullary rays being very rare. The fibres vary in form according to their position in the annual rings of the tree, the tracheids of the spring and summer wood, which are present in predominant proportions, being relatively broad, flat, and thin-walled, with rounded or bluntly pointed ends, whilst those of the autumn wood are thicker-walled and fusiform, with pointed ends. The tracheids of the *Coniferæ* are definitely characterised by the presence of circular pores disposed longitudinally and surrounded by circular depressions or pits; plain pores, broadly oval in shape, are also present in fibres of the genus *Pinus*. In some cases these pores are seen in profile, and give the edges of the fibres a characteristic serrated appearance. Some of the thick-walled type of fibres show a very pronounced reticulated structure in their walls, resembling that observed in the cotton fibre. The fibres of the dicotyledonous woods, of which poplar is the type, are quite short and definitely fusiform, with fairly thick walls and a few narrow slit-shaped pores disposed diagonally. Some of the fibres of poplar pulp have nodes at regular intervals like those sometimes present on linen fibres. These pulps are at once identified by the presence of very broad vessels with extremely thin walls. These vessels are open at both ends, and are covered with pores, arranged in beautifully delicate patterns, which serve to some extent to distinguish between the different kinds of wood from which the pulp has been prepared.

In *mechanical wood pulp* the individual fibres described above are rarely found intact and isolated; they occur either as mutilated fragments, or as broken aggregates of several fibres held together by transverse bonds consisting of the medullary rays. Mechanical wood pulp consists essentially of a ligno-cellulose, resembling the jute fibre in most of its chemical properties. (See p. 64.)

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Below are diagrams showing the microscopical characteristics of representative wood fibres.

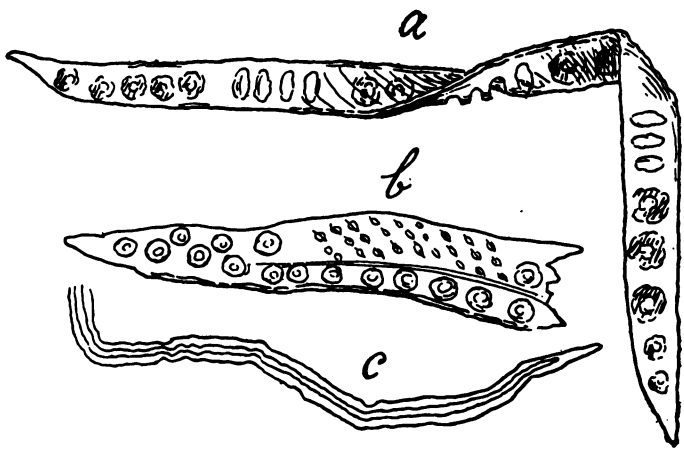

FIG. 15.—TRACHEIDS FROM CONIFEROUS WOOD (SULPHITE WOOD PULP.)

a, Summer tracheid of pine wood (*Pinus*); *b*, summer tracheid of spruce wood (*Abies*); *c*, autumn tracheid.

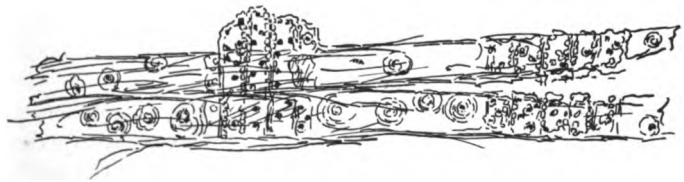

FIG. 16.—MECHANICAL WOOD PULP FROM SPRUCE. Tracheids united by transverse cells of medullary rays.

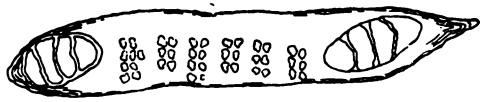

FIG. 17.—VESSEL FROM DICOTYLEDONOUS WOOD PULP (AMERICAN POPLAR).

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CHAPTER V.

SPECIAL TREATMENT OF VARIOUS FIBRES; BOILERS, BOILING PROCESSES, ETC.

We have already discussed the principles upon which are based the chemical treatments of the various fibres for the isolation of cellulose, or of a partially purified fibre suitable for paper-making; of the two groups of processes, alkaline and acid, the former largely preponderate, fulfilling as they do a much wider range of conditions and attacking all the compound celluloses. The acid processes are for practical purposes limited at present to the treatment of woods by the bisulphites of lime and magnesia. The alkaline processes have the considerable economic advantage of allowing, by simple means, the recovery of the alkali. The waste liquors from the processes, when soda is used, are evaporated to a point at which the residual water does not prevent combustion of the organic matter, the burning off of which takes place in furnaces of various construction. The soda is thus recovered as carbonate ('recovered ash'), or sulphide and is available for further use.

The practice of these methods of recovery is obviously limited by the degree of dilution of the soda, whether in the liquors as obtained directly from the boiler, or in the wash waters from the 'boiled' pulp.

We now proceed to consider each fibre in detail, giving at the same time such information as is necessary regarding the preliminary treatment of the various fibres, and describing the forms of apparatus in which these operations are conducted. We shall consider the fibres in the order of their simplicity of treatment.

Rags (Linen and Cotton).—The treatment necessary for

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rags differs largely according to their quality and, of course, according to the kind of paper for which they are intended. The different qualities are known in the trade by different names and marks, such, for example, as the following :—New linen pieces, new cotton pieces, superfines, dark fines, grey linen, sailcloth, seconds, thirds, etc.

The two former consist of the cuttings produced in the manufacture of various garments, etc.; not having been worn, they are usually free from dirt, and are, in fact, if bleached, nearly pure cellulose, containing only the starch and other sizing material which have been added in the process of finishing the goods. They may, of course, contain considerable quantities of china clay or other loading material. In purchasing rags, therefore, regard should be had to the probable presence of these bodies. Such rags require only a very slight treatment; in fact, for certain classes of paper, they might be used without any preparation. If, as is sometimes the case, the rags are unbleached, a rather more severe boiling is necessary.

It may be noted here that the removal of starch from 'rags,' i.e. cuttings of unused cloth, whether bleached or unbleached, is by no means easily accomplished by the ordinary alkali boil. The first effect of the treatment being to gelatinise the starch, which then combines with the alkali, the penetration of the rags by the alkaline lye is much impeded. The starch is best attacked by the specific treatment of malting. The rags are boiled with sufficient water to swell the starch; more water is then added to cool the mass to 60° C., and an infusion of malt is then added. In 1–2 hours the hydrolysis of the starch is so far complete that the ordinary boiling may be proceeded with after adding the complement of alkaline lye.

The greater part of the rags used in paper-making, however, consist of the residual portions of garments, household linen, etc., which vary in quality from clean, almost unused portions, to the very foulest sorts; the latter require a very drastic treatment. The first thing to be done with the rags is to 'sort' and cut them into convenient pieces. This is usually done by women, who stand at tables furnished with broad knives firmly

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fixed into them, with the backs towards the worker, and inclined at a slight angle. Near to the women are placed a number of boxes, corresponding with the number of qualities of rags, lined at the bottom with coarse wire gauze, into which the different sorts are put. The distinctions made are more or less arbitrary,

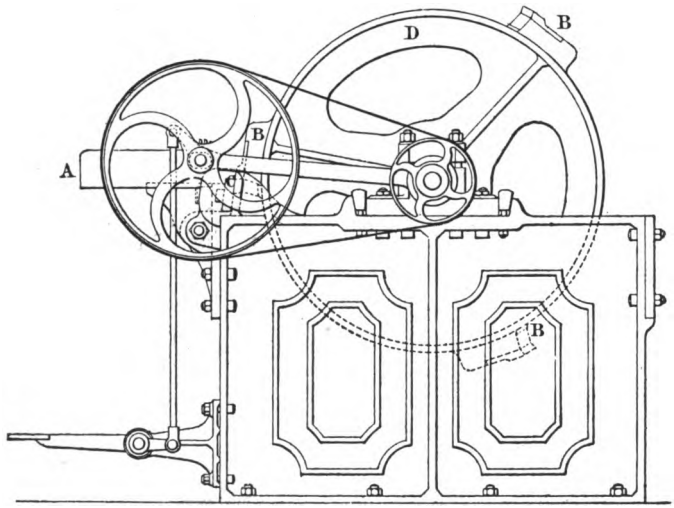

FIG. 18.

but as a general rule the rags are sorted with special reference to their colour, strength, and the material of which they are composed, which in turn are essential factors of the degree of chemical treatment required. The coloured rags may be allowed to accumulate, and then made into a coloured paper. During the process of cutting, all hard substances, such as buttons, pieces of iron, etc., are carefully removed. The rags are cut into pieces of from two to five inches square. In some mills machines are used for cutting.

Fig. 18 shows the construction of a machine that may be used either for rags or rope. The material is passed into the machine along the table A, where it passes between the station-

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ary knife C and the knives B, fixed in the revolving drum D. The cut rags fall into a receptacle placed underneath the drum.

Notwithstanding the extra expense of cutting by hand, it is nevertheless preferred by many, especially for the finer grades of paper. One reason for this is to be found in the fact that more perfect sorting and removal of impurities can be effected. It is moreover said that less waste of fibre occurs in the subsequent operations.

The next process which the rags undergo is that of removing all loose extraneous matter. This may be done in a machine such as is shown in Fig. 19. The rags are fed con-

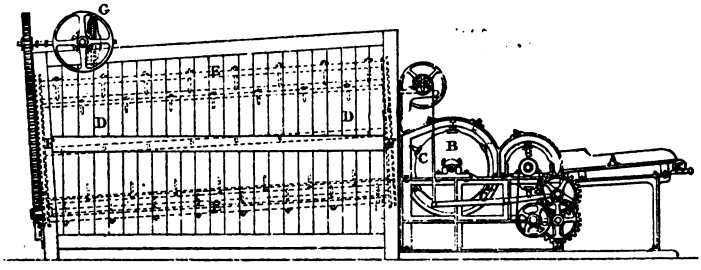

FIG. 19.

tinuously by the endless travelling platform A into the willow. This consists of two wrought-iron drums, B B, furnished with wrought-iron teeth C, which, when the drums revolve, pass rapidly near to the stationary teeth fixed into the cast-iron framework of the willow. The sides are covered in with cast-iron doors, and the top is covered over with sheet iron. Underneath the drums is a grating for the escape of dust.

The rags, having been thoroughly beaten by the teeth of the drums, pass into the duster D, consisting of a kind of hollow cylinder E, made of strong iron bars securely fastened to the circular ends F, the bars being covered with wire cloth or perforated zinc. It is made to revolve almost horizontally, a slight dip being given to it in order that the rags may be carried forward to the lower end. The bars or skeleton of the cylinder

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are furnished with a number of teeth securely bolted on. The whole is inclosed in a strong wooden box in which it revolves, and which serves to collect the dust passing through the wire cloth. The cylinder E is driven by the gearing G. This combined willow and duster may be used for dusting and cleaning not only rags, but almost any other kind of fibre. The willow and duster sometimes form two separate machines.

The cleaned and dusted rags are now ready to be boiled, although it is the practice in some mills to give them a preliminary washing with water.

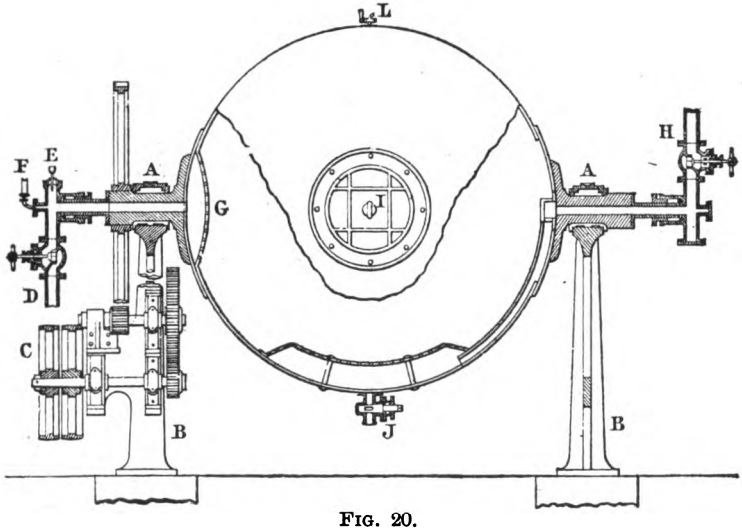

FIG. 20.

The boiling may be conducted either in spherical or cylindrical boilers, or in the ordinary vomiting boilers described under Esparto. (See p. 128.)

In Fig. 20 is shown, part in section and part in elevation, a spherical rag-boiler, as manufactured by Messrs. G. and W. Bertram. This boiler, of from 8 to 9 feet diameter, is supported by means of the hollow journals A on the standards B and is made to revolve by means of the gearing C.

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Steam enters by the pipe D, which is fitted with a safety-valve E, and vacuum valve F. The steam on entering the boiler is distributed by means of the 'baffle-plate' G. Lye enters by the pipe H. The boiler is fitted with two doors I, wherewith to fill and empty; the waste lye is run off by the cock J. L is a small blow-through cock. The false bottom prevents the rags from choking up the cock, and also serves to drain off the waste liquor.

The alkali employed may be either caustic lime, caustic soda, sodium carbonate, or a mixture of the latter and lime, which is of course equivalent to using caustic soda. The proportion of alkali depends upon so many considerations that it is qnite impossible to give exact information on this point. In the case of caustic soda, a quantity equal to from 1–5 p.ct. on the rags may be taken to be a fair average. If lime be used it should be slaked with water, made into a thin milk, and carefully filtered through fine wire cloth to keep back the particles of sand, coal, etc., which lime is always liable to contain. From 5–10 p.ct. may be used. The amount of lime actually dissolved in the water is relatively small (1·3 grm. per litre); the portion in solution, however, rapidly combines with the grease, dirt, and colouring matter of the rags and forms with them insoluble compounds, a fresh portion of lime being at the same time dissolved. This formation of insoluble compounds constitutes an important objection to the use of lime, as they are liable to remain to some extent fixed in the rags, and are with great difficulty removed by washing. For this reason, therefore, the more soluble alkali is to be preferred. Moreover, the lime sometimes tends to exert a hardening effect upon the cellulose. Notwithstanding these objections, lime is used by some paper-makers in preference to soda. In making choice of the chemical for boiling, much depends on the quality of the rags and the nature of the paper for which they are intended; so that no fixed rules can be given.

To reduce the treatment of rags to 'first principles,' the paper-maker requires to inform himself of the chemical treatments adopted in the textile industries, whether in *bleaching*

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the goods or in dyeing and printing them. As regards the former, he requires to follow the same line of treatment; and in the removal of colour from dyed and printed goods, a knowledge of the method by which the colour was fixed will enable him the more economically to undo that process.

The time of boiling varies from 2 to 6 hours, according to the quality of rags, the chemical employed, and the pressure. The use of very high pressures should be avoided as far as possible, as there is a danger, owing to the correspondingly high temperature, of *fixing* the dirt and colouring matters instead of dissolving them.

The quantity of water should be kept as low as may be, in order to have as strong a solution of alkali as possible; this effects a saving both in the time of boiling and in the alkali, and this is of great importance where it is necessary to evaporate the whole of the waste liquors. It should also be remembered that a certain amount of water is always formed by condensation in all boilers in which live steam is used. On the other hand, if too little water be added, the rags are liable to become 'burned' and the fibre therefore weakened. During the operation the boiler should be made to revolve slowly, in order to produce thorough circulation of the liquor.

The boiling being completed, the pressure is allowed to fall either by cooling or by blowing off from a cock usually provided for that purpose, and the liquor allowed to collect at the bottom of the boiler. It is then run off by the cock J (Fig. 20), and the rags drained as much as possible. Water is then run in to give the rags a preliminary washing. For the better elimination of grease (soap) the water used for this first rinsing should be heated by means of steam. After again draining, the rags are withdrawn from the boiler into any suitable receptacle. A convenient form is that of a rectangular iron box on wheels, which can be readily transferred from one part of the mill to another.

The next process is that of washing. This is usually performed in a washer or breaker, the construction of which is shown in Fig. 21.

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It consists essentially of a rectangular vessel with rounded ends, in the centre of which, but not extending the whole way,

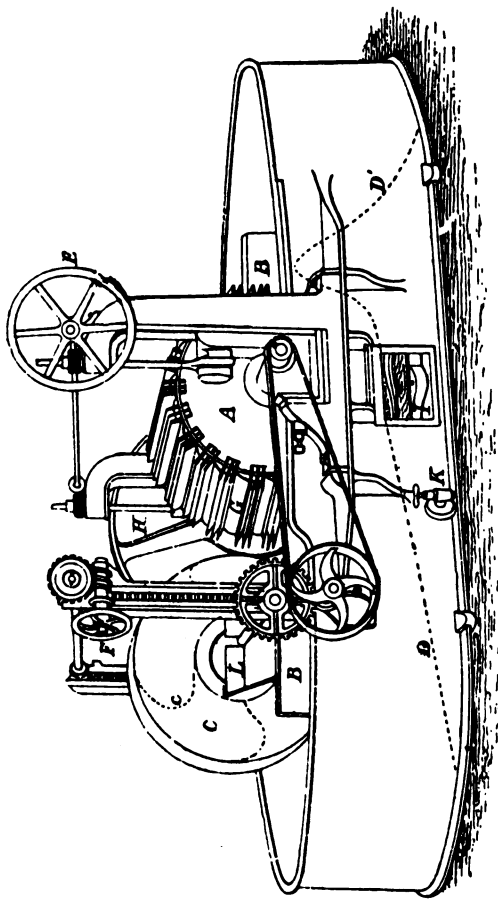

FIG. 21.

is a partition B, known as the 'mid-feather.' The roll A, which is furnished with a number of steel knives G, and driven

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from the wheel H, revolves in one of the compartments formed by the mid-feather. In this compartment the floor is inclined in such a way as to bring the pulp well under the roll, as shown by the dotted line D. Immediately under the roll is what is called the 'bed-plate,' the end of which is seen at I, extending up to the mid-feather, and fitted with knives similar to those in the roll A. The arrangement of the knives, both in the bed-plate and the roll, is similar to that given in Figs. 33 and 35. The distance between the roll and the bed-plate can be varied at will by means of the handle E, which is so arranged as to raise both ends of the roll simultaneously. In those breakers of an older pattern, one end only of the roll was raised, and thus the knives became worn unequally.

After passing between the roll and the bed-plate, the pulp flows down the 'back-fall' D', and finds its way round to the other side of the mid-feather. On the inclined part of the floor, and immediately in front of the bed-plate I, a small depression is made, covered with an iron grating, for the purpose of catching buttons, small pieces of stone, and other heavy substances that may have found their way into the rags. There is generally a similar grating with rather finer openings on the other side of the mid-feather. The engine is constructed of iron, generally made in one casting.

The dirty water from the rags is removed by the 'drum-washer' C. It is divided into compartments by the bucket-shaped partitions shown by the dotted line *c*. The centre of the drum is formed of a conical tube, the narrow end of which is towards the mid-feather, and the water lifted by the buckets is discharged through this tube. The ends of the drum are generally made of mahogany, as this is found to stand the action of alkali better than any other wood. The periphery is covered with fine copper or brass wire-cloth, laid on to a backing of a much coarser material. An improved form of backing has been introduced lately, which is much more durable than wire. It is formed of brass cut into the form shown in Fig. 22. The drum can be raised or lowered by the small wheel F, and it is driven by a belt on the shaft that bears the roll.

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The wash-water passes through the wire-cloth into the compartments formed by the partitions *c*, and finding its way down to the narrow end of the inner conical tube, flows out through the side of the drum into a trough which is placed across the washer to receive it. Or it may, as shown in the drawing, be conducted through the mid-feather itself, which is made hollow at this part for the purpose.

The water passing through the wire-cloth on the drum carries with it a certain amount of fibre, which, unless special precautions are taken (see 'Save-all,' p. 235), is lost. The amount is considerable in the case of weak rags, and care should

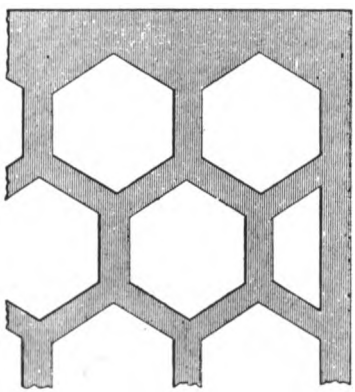

FIG. 22.

therefore be taken that the washing is not prolonged more than is consistent with proper cleansing, and that the pulp should not be too much broken up at this stage.

The washed and broken pulp goes by the name of 'half-stuff.'

The operations of washing and breaking the rags and beating to 'half-stuff' are generally carried out somewhat in the following manner. The engine is first half-filled with water, and the damp rags from the boiler are put in gradually until the trough is nearly full. The mass is got into circulation during the process of filling, the movement of the rags being assisted by

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working them about with a wooden paddle. Water is now allowed to flow in at the end of the trough furthest removed from the drum-washer, and is so thoroughly mixed up with the pieces of rag under the action of the roll, that it extracts all the soluble matters and carries away with it most of the fine insoluble impurities. The rate of admission of fresh water is adjusted so as to be equal to the rate of discharge of foul water through the drum-washer, and the level of liquid in the engine is maintained constant. In the case of strong, hard rags, when thorough circulation of the full charge has been established, the roll is lowered on the bed-plate for a short time in order to produce a number of cuts on the rag-pieces, without, however, separating them into small fragments. This opens out the fabric of the rags, and facilitates the removal of the dirt and impurities: with soft, or weak rags, on the other hand, such a treatment is neither necessary nor desirable. During the washing operation which follows, the roll is kept well off the bed-plate, and the rags are circulated until the wash-waters come away nearly clear. It is important that no considerable degree of 'pulping' should take place until most of the suspended impurities have either settled in the button traps situated in the floor of the engine, or have been removed through the washing-drum, otherwise particles of these will become entangled in the pulp and will appear as specks in the paper. The roll is then cautiously lowered until the pieces of rag can be just felt passing between the roll and the bed-plate. The object at this stage is to pull out and separate the ultimate fibres from the loose ends of the threads, which are exposed at all the cut edges of the fabric, by drawing the rags against the resistance offered by the knives of the bed-plate, whilst avoiding actually cutting the cloth by direct shearing strokes.

The strength of the ultimate fibres and the toughness of the cloth determine the fibre-length of the 'half-stuff' so obtained. The object in beating to 'half-stuff' is to reduce all the different grades of strong and weak rags to an approximately equivalent condition in order that a mixture of the various 'half-stuffs,' shall behave as a homogeneous mass in the subsequent operation of beating to 'whole-stuff.'

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Before the reduction of the rags is complete, the water issuing from the washing-drum will have become perfectly clear, the supply of fresh water is then stopped and the drum is raised out of the pulp by means of the handle F. As the pieces of rag become more and more resolved the weight of the roll is allowed to bear more and more on the bed-plate, until at the end it is exerting its full pressure. Meanwhile, the washing-drum is again lowered into the pulp and the excess of water in the engine is thereby removed until the pulp is concentrated to a suitable degree. In cases where the 'half-stuff' is to be bleached, the necessary quantity of strong, bleach liquor may be added to the engine shortly before the pulp is ready. The bleach is thoroughly worked in by the action of the roll and the 'half-stuff' is discharged into chests fitted with perforated bottoms through which the water is drained off after the action of the bleach is completed. In other cases bleaching is carried out in separate engines or 'potchers' provided with circulating paddles or screws, the action of which accelerates the process. The process of bleaching will be described in Chapter VII.

The bleaching process is often completed in the 'beater' itself, but this is not to be recommended.

Esparto.—This raw material, on account of its high percentage of non-cellulose constituents, requires a large amount of soda to resolve it; on the other hand, being of the nature of a pecto-cellulose, the process of disintegration may be conducted at a low pressure; in fact, it is the practice at some mills to boil in open vessels, in which case, however, a larger amount of soda is required. As has been already stated, it may be taken as a general rule for all fibres, that within certain limits the higher the pressure employed the less soda is required. The quantity necessary again varies with the various qualities of esparto, which depend in the first instance upon the country or district of origin of the grass. Caustic soda is the chemical invariably employed; lime, on account of its forming insoluble compounds with the non-cellulose portion of the grass, is inapplicable. Not only does the amount of soda depend upon the pressure, but it also depends to a considerable extent on the form

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of boiler employed. The use of rotary boilers is objectionable, as the esparto tends to collect together into compact masses, which are with difficulty penetrated by the liquor. It is therefore the almost universal practice to employ stationary boilers, in which an automatic circulation of the alkaline lye is maintained on what is technically known as the 'vomiting' principle.

The first treatment that the esparto undergoes is that of 'picking.' The bands of the bales in which esparto is packed, generally by hydraulic pressure, are cut, and the grass is spread out on tables by women, who carefully remove such impurities as weeds, root-ends, etc., which from their

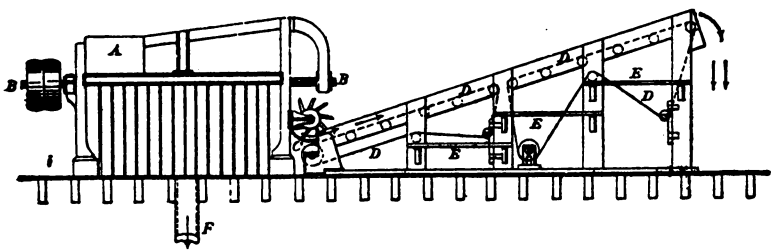

FIG. 23.

nature are with great difficulty boiled and bleached, and which if not removed would be liable to appear in the finished paper as dark-coloured specks, technically known as 'sheave.' This treatment is called 'dry-picking,' in contradistinction to a subsequent process, known as 'wet-picking.' A portion of the table is covered with coarse wire gauze, through which, when the grass is spread over it, loose particles of sand, dirt, etc., escape. The cleansing of esparto can be much better accomplished by means of machinery. Fig. 23 is an elevation of a machine manufactured for the purpose by Messrs. Masson, Scott and Bertram. The grass, which may be in the form of sheaves, as taken from the bales is put in by the hopper A. It passes thence to a conical drum made of steel bars placed very close together, driven

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rapidly by the shaft B. It is provided with five rows of teeth. Fixed to the sides of the willow there is also a row of stationary teeth. The grass is thoroughly broken up and dusted by the action of the teeth, and is transferred to the wide end of the willow at C, where it is carried forward on the travelling tables D. During its passage along the tables it can be examined and picked by women standing on the platforms E. The dust and dirt passing through the steel bars of the drum are drawn away by a fan through the pipe F.

In more recent practice the hand-picking, both dry and wet, is disappearing, and is being replaced by the 'presse-pâte' system (see p. 133), in which the dirt and underboiled portions of the grass are removed mechanically by means of sand-tables and strainers. In this case the picking-platforms E are done away with, and the dusted grass is conveyed from the willow to the boiler-house. It is taken forward by means of travelling rakes over the tops of a series of boilers, any one of which can be furnished by simply opening a door corresponding in position with the lid of the boiler.

Boiling.—The ordinary form of boiler is shown in Fig. 24. It is known as a vomiting boiler. The grass is put in by the door E, which is hinged and is counterbalanced by the weights L. It is securely fastened down by the screws F. Steam enters by the inner pipe A, which dips a little below the perforated false bottom B. Surrounding the steam pipe is a wider pipe C, open at the top, which is made slightly trumpet-shaped, also open at the bottom, where it ends in a kind of shoulder, on which the false bottom rests. The lower part has two or more openings G cut away, through which the liquid can freely pass.

In order to get as large a charge into the boiler as possible, steam is turned on while furnishing, and a quantity of caustic soda lye is also run in, which has the effect of softening the grass and making it more compact. This is continued until the boiler is well filled.

The action of the boiler is as follows:—the steam passing

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through the pipe A, heats the liquor that has drained from the grass through the perforations in the false bottom, and, forcing it up the wide-pipe C, causes it to strike against the dome or bonnet D, and distribute itself again over the grass. This constitutes the 'vomiting' process of circulation of liquor.

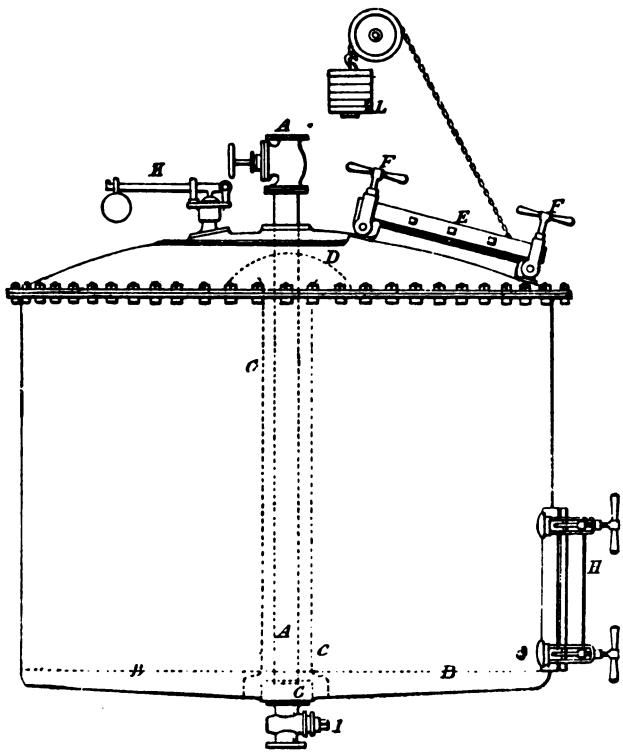

FIG. 24.

The boiler is emptied by the door H, and the liquor is run off by the cock I. The boilers are usually supplied with a safety valve K, and also with a pipe for letting off the steam when the boiling is finished. The boiling generally takes

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from 4 to 6 hours. The quantity of soda necessary depends upon the nature of the grass, Spanish requiring less than African.

Routledge, to whom the introduction of esparto as a paper-making material is due, gives 10 p.ct. as the proper quantity.

The pressures employed vary from 5 lb. to 45 lb. There has been a growing tendency of late to employ the higher pressures, for reasons already stated.

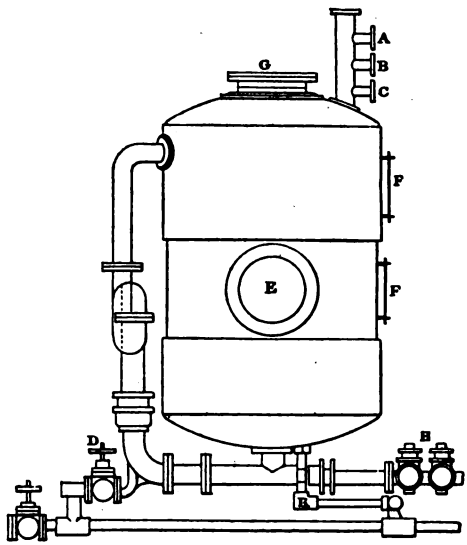

FIG. 25.

Of late years, great improvements in the form of the boiler have been introduced. Fig. 25 is an illustration of Roeckner's Patent Boiler. The vomit pipe is outside the boiler. Steam entering by the cock D, forces the liquor up the vertical vomit pipe and distributes it over the grass. The pipe K is used for heating the liquor at the commencement of the operation by means of waste steam. F F are gauges for indicating the height of the liquor. The grass is put in by the opening G. The

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pipes, A, B and C are for the supply of steam, strong lye and water. The boiled grass is discharged by the circular door E.

The boiler holds three tons of grass, and the boiling is completed in 2–3 hours, the pressure being about 35–40 lb. per square inch. It is claimed that by its use a saving both of time and soda is effected.

Sinclair's Patent Boiler, which is the type most generally employed at the present time, is shown in Fig. 26. The vomit pipes, of which there are two, are made of thin steel plates riveted to opposite sides of the boiler. The liquor drains through the perforated false bottom, and is then forced up the vomit pipes above the perforated plates, through which it is distributed over the grass in a number of fine jets. The boiler is charged by the door *e* and emptied by *j*. The small cock *a* is used as a blow-through cock; the opening *b* is used for blowing-off steam when emptying the boiler; *c* for letting in caustic soda lye; *d* for water. Steam enters by the small branch of the T pipe at the bottom of the boiler, the other, *g*, being used for running off the waste liquor. A boiler holds from two to three tons of grass, and a boiling is completed in about two hours at a pressure of 40–50 lb. per square inch. Under these circumstances it is easy to conduct four complete operations in one boiler in the twenty-four hours; the time required for filling and emptying being one hour each.

The two forms of boiler above described possess the obvious advantage of having the whole or nearly the whole of the interior available for holding grass; the boilers can therefore be made to hold more, and the boiling is moreover much more evenly accomplished.

Washing.—The boiling being completed, the steam is allowed to escape and the liquor to collect at the bottom of the boiler, where it is run away by the pipes placed at the bottom for the purpose. Water is then run in and steam turned on for a short time; this is also run off, and the grass drained as completely as possible. The boiled grass is then emptied into trucks and taken away to the washing engines. These resemble those already described under Rags.

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During the process of washing, a certain amount of the shorter fibres find their way through the meshes of the wire-cloth. In addition to this, a large proportion of the cellular

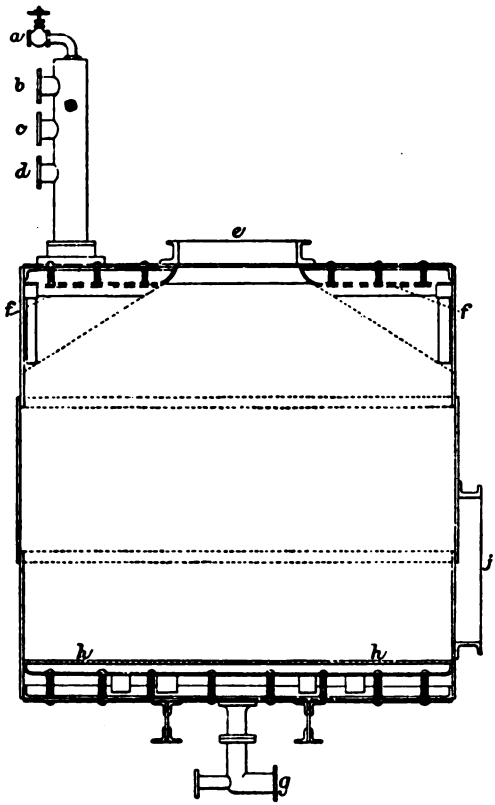

FIG. 26.

tissue surrounding the fibro-vascular bundles (see Fig. 10, p. 106) is carried away. If the wash-water be examined under the microscope, it will be seen to consist largely of this cellular matter. Though this entails a certain loss of cellulose, its

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removal is in other respects advantageous, as it is possessed of hardly any 'felting' properties, and it is exceedingly difficult to bleach.

The amount of fibre actually obtained in practice is but little below that contained in the grass. A certain loss is inevitable, but this probably does not exceed 1 or 2 p.ct.

The percentage of cellulose in esparto is given on p. 108. The following numbers obtained by the authors are somewhat higher. They are calculated on the absolutely dry fibre; those mentioned are on the *air-dry* samples:—

	Cellulose per cent.
Spanish.	58·0
Tripoli	46·3
Arzew	52·0
Oran	45·6

There is no doubt that considerable differences occur even between different specimens of the same kind of grass.

It is the practice in some mills to wash the grass in a series of tanks connected together in the same way as the lixiviating tanks of an alkali works. They are so arranged that pure water flows in at one end, passes through fresh lots of grass in succession, and issues at the further end highly charged with the soluble products of the grass. By such an arrangement the grass can be washed without any loss of fibre, and with a minimum quantity of water. This latter feature is of great importance in mills where it is necessary to evaporate the whole of the waste liquors from the esparto, as they are then obtained in a very concentrated form. Even with such an arrangement it is advisable to give the grass a short final treatment in the washing engine.

We may mention here Messrs. Masson and Scott's patent 'Tower' system of treating esparto, although it is also applicable to other pulps. In this system, the washing, breaking and bleaching are performed in one continuous apparatus. This consists of a series or 'battery' of tower-shaped vessels, generally constructed of expanded steel-work and cement, cylindrical in form and of considerable height, tapering to a point at the bottom. Owing to this particular shape, a large number of

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vessels of large capacity can be provided on a relatively small floor-space. At the point of the conical bottom of each 'tower' is placed a centrifugal circulating pump, the vanes of which exert sufficient friction on the grass to bring about the resolution of the fibre-bundles. The pulp is withdrawn from the bottom of the 'tower,' and is discharged by the pump through an ascending pipe on to a conical distributing plate in the upper portion of the 'tower.' When necessary, the pulp, as it is delivered at the top of the 'tower,' can be made to pass through a vat containing a drum-washer before it it is discharged on to the distributing cone, whereby the soluble purities are eliminated. The discharge pipes of the circulating pumps are so arranged that the pulp can be circulated continuously through the same 'tower,' or diverted to the next 'tower' of the series.

The washing having been completed, and the esparto having been broken up into 'half-stuff,' it is now ready to be bleached (see Chap. VII.).

The presse-pâte system, originally adopted for the treatment of straw, has of late years been extensively applied to esparto.

The presse-pâte consists of the wet end of a paper machine, and is furnished with sand-tables and strainers. The pulp is allowed to flow on to the wire cloth, so as to form a thick web of pulp. The bulk of the water passes away through the wire cloth; a further quantity is removed by the vacuum-boxes and couch-rolls. The pulp, containing from 50 to 60 p.ct. of water, is wound round an iron rod until a sufficiently large roll is formed.

The advantages of the presse-pâte system are the possibility of the removal of dirt and unboiled portions by means of the sand-tables and strainers, and the very complete washing and removal of the products of the action of bleaching powder.

It also enables manufacturers to dispense with the somewhat costly methods of dry and wet picking.

The presse-pâte system can also be applied to the unbleached pulp.

It may be interesting at this point to say something about the substances which are removed from the esparto by the caustic soda. On referring to p. 108, it will be seen that the original

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grass contains nearly half its weight of non-cellulose, the removal of which has to be effected. Only a small proportion of this is 'extractive matter' in the ordinary sense of the term, i.e. that can be extracted by the usual solvents; the remainder is intimately combined with the cellulose. The action of the caustic soda is to resolve these bodies, the cellulose remaining behind, and the other constituents being dissolved as 'resinous' bodies by the soda. A certain proportion of the mineral constituents, notably the silica, dissolves in the lye, the latter forming silicate of soda.

On neutralising the liquor with an acid, the bulk of the dissolved constituents is thrown down as a dark brown resinous mass. If this crude product be purified, it is found to consist of a definite body having the formula $C_{21}H_{24}O_8$. By the action of chlorine on this resin a bright yellow chlorine compound is formed, resembling the compound from jute described on p. 58. If the resin be treated with concentrated nitric acid, a bright yellow body is formed, which forms definite compounds with bases, and which has the property of dyeing animal fibres a bright orange colour. In addition to this body, a yellowish-white wax can be isolated. It sometimes happens that this wax is but imperfectly dissolved in the caustic lye; if the waste liquor be allowed to stand, the wax is occasionally found to collect in small quantities on the surface.

Various attempts have been made from time to time to remove from the waste liquors the soluble matter derived from the esparto by the addition of lime. This throws it down, in fact, as a very voluminous precipitate, exceedingly difficult of filtration. The filtrate contains only caustic soda. The difficulties of removal of the precipitate, however, are almost insurmountable. The usual method of disposing of the liquor is to evaporate it to dryness and ignite it, and will be subsequently described under the head of 'Soda Recovery,' Chapter XI.

Another by-product deserving specific mention is acetic acid, which is formed to some extent in the boiling process, but in much greater proportion in the further evaporation of the liquor, and charring the residue. The production of acetate is a maxi-

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mum when the temperature of charring does not exceed 350°. The acetic acid is obtained as sodium acetate on lixiviating the char, the yield of the salt amounting to 5–6 p.ct. of the weight of the original esparto. Such a process was patented by W. H. Higgin in 1891,* and the above results verified by operations on the large scale. But the process has not been practically adopted.†

Straw.—Straw very closely resembles esparto in its chemical constitution ; it is, however, more highly lignified, and for this reason (see p. 60) requires a more drastic treatment for its resolution. It is therefore usual to treat straw with rather larger quantities of caustic, and generally at high pressures. It is possible, however, to resolve it at 5–10 lbs. pressure, but the resulting pulp is more difficult to bleach, and can only be used for inferior kinds of paper. In treating straw for use in high-class paper, i.e. for the isolation of a 'pure' straw cellulose, it is necessary to boil under such conditions that even the knots, which are much less readily attacked, shall be so far disintegrated that they may be bleached with a moderate quantity of bleaching powder. Such a treatment, on the other hand, involves a diminished yield of pulp, and at the same time a somewhat weakened fibre.

The kinds of straw in general use are wheat, oat, rye, and barley ; the two first constituting the bulk of the raw material, at least in this country. Some idea of the composition of straw may be gathered from the analyses given on p. 110.

It will be seen that the amount of cellulose is quite as high as in esparto, but for the reasons above given and from the fact that a large proportion of the cellulose consists of cellular tissue (see Figs. 12 and 13), which is easily attacked by soda and readily passes through the meshes of the drum-washers and the wire-cloth of the presse-pâte and paper machine, the yield obtained in practice falls considerably below that from esparto.

* English patent 13,409.

† See also 'On the Production of Acetic Acid from the Carbohydrates,' Journ Soc. Chem. Ind. **5**, 11.

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In addition to the numbers already quoted on p. 110, the following results of analyses made from time to time by the authors, may be interesting. The percentages are calculated on the absolutely dry material.

	Cellulose per cent.
Oat straw	52·0
,, ...	53·5
Wheat straw	49·6
Rye ,, (foreign) . . .	53·0
Oat ,, ,, . . .	46·5
Wheat ,, ,, . . .	50·2

The yield of pulp is greatly influenced by the conditions under which it is obtained; high pressures and temperatures exerting considerable influence on the result. This is probably the case with straw more than any other fibre, on account of the physical and chemical nature of the cellulose. It is doubtful whether much more than 35 p.ct. is actually obtained in practice.

Straw is usually boiled in cylindrical rotary boilers. Some paper-makers, however, prefer to use one or other of the different forms of vomiting boilers already described.

The use of a rotary boiler is open to certain objections. In the first place, it is doubtful if they are as economical of soda as the vomiting boilers, especially the more recent patterns; and, secondly, the rotation of the boiler so disintegrates the pulp, that a certain proportion of the cellulose, especially those fibres which are short, is liable to be lost during the subsequent treatment. It seems probable that the best results would be obtained if the rotation of the boiler were reduced to a minimum, in fact, sufficient only to produce thorough circulation of the liquor.

The proportion of soda necessary to boil straw thoroughly is, for reasons already stated, greater than is the case with esparto. The amount varies from 10 to 20 p.ct. on the raw material.

The different processes to which straw is subjected vary greatly. The following may be taken as a general indication of the methods employed. The straw is usually cut into short

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pieces of about 1–2 in. in length by means of an ordinary chaff-cutter. The cut straw is carried by means of a blast of air along a wooden tube or shaft into a chamber, the sides of which are made of coarse iron gauze. This chamber is itself enclosed in another chamber, in which the dust and dirt accompanying the straw collect. The clean straw is then placed in sacks and conveyed to the boiler-house.

Owing to the bulky nature of straw, it is difficult to get a large charge into a boiler at one operation; it is therefore usual, after having filled it as completely as possible, to run in a portion of the lye required, and to turn on the steam for a few minutes. This has the effect of so far softening the straw as to make it lie closely at the bottom of the boiler and to allow of a further quantity being put in. This having been accomplished, the remainder of the lye required is run in, together with the requisite quantity of water, and the steam turned on. The pressure may vary from 10 to 50, or even 80 lbs. per sq. in., and the time from 4–8 hours.

When the boiler has sufficiently cooled, the charge is run out by a cock in the bottom. Owing to the rotary action of the boiler the straw is in the state of fine pulp, having been almost completely disintegrated; so fine, in fact, that it flows readily through a 3-in. pipe. It is run into large tanks with perforated tile bottoms, where the excess of liquor is allowed to drain away and the pulp washed by the addition of water. It is then dug out and taken to be bleached. Before this is done, however, it may be necessary to give it a further washing. This may be done in the potcher itself. Instead of washing the straw in tanks, it may be washed in an ordinary washing engine, such as has been already described. Owing to the finely divided state of the pulp, however, this method, unless the meshes of the wire-cloth covering the drum-washer are very fine, entails a considerable loss of fibre. It is more suitable in cases in which therefore it is less disintegrated. When stationary boilers are employed, it is not necessary to cut the straw very fine; in fact, it is sometimes put in the boiler whole. The cutting has this advantage, that it loosens the adhering dirt. In cases where

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the action of the soda has not been carried far, or the straw has been put into the boiler whole, the pulp will not be disintegrated to the same extent, and will not flow through a narrow pipe. It is necessary therefore to discharge the boiler through the doors used for filling.

A novel form of washer especially adapted for straw, whereby the washing is effected with the minimum quantity of water has been used on the Continent to a considerable extent, and in some mills in this country. The pulp is caused to pass along a series of revolving cones covered with wire-cloth, through which the liquor escapes. As it reaches the end of each cone, the pulp is emptied into a small tank containing water from the cones further on in the series. It is carried forward by means of hollow bent arms connected with the inside of the next cone, which then discharges it at the other end, to be again carried forward.

As already stated, the presse-pâte system is largely adopted for straw pulp; it has been described under Esparto. It may sometimes be employed with advantage before bleaching, though it is generally used after.

A method of treating straw is sometimes adopted which produces a pulp of higher quality than is obtainable by the ordinary method. The washed pulp is mixed in a chest provided with stirrers, with a large quantity of water, and is then pumped into another chest placed at a higher level, from which it flows between a pair of hard granite mill-stones, the surfaces of which are cut into radial grooves. The stones are fixed horizontally, and are made to revolve at a very rapid rate. During the passage of the pulp through the stones, the knots, weeds and other hard portions of the straw which may have resisted the action of the alkali are reduced to a fine state of division, and are thus more readily acted upon in the subsequent operation of bleaching. The degree of fineness to which the pulp is reduced can be determined by regulating its flow and the distance between the stones. Pulp produced in this way is of a very even character, and is comparatively free from unbleached particles.

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Within recent times a process of treating straw has been introduced which, on account of the high quality of the pulp produced, has attracted considerable attention from paper-makers. It consists in exposing pulp obtained in the usual way by the action of caustic soda, to the action of chlorine gas.* The amount of soda in the preliminary boiling is reduced much below that necessary for perfect pulping, the result being that the cellulose is much less liable to be destroyed, and thus a greater yield is obtained. The pulp is thoroughly washed and partially freed from moisture in a centrifugal machine until only about 70 p.ct. remains. The partially dried pulp is then exposed in leaden or stone chambers for some hours to an atmosphere of chlorine, produced by the action of hydrochloric acid upon manganese dioxide. By the action of the chlorine, those portions of the straw which have been but imperfectly acted upon by the caustic soda in the boiling process are completely disintegrated, or, rather are rendered more susceptible to the action of the bleaching liquor employed subsequently. The consequence is that when bleaching liquor is added, the whole of the straw is rapidly reduced to the state of pure cellulose, and the finished product is remarkably free from anything like unbleached portions. Owing to the fact that the action of the caustic is minimised, a considerable portion of the more easily degraded cellulose survives, and the yield of the pulp is thereby increased. The process is, however, necessarily expensive. The action of the chlorine will be readily understood by a reference to p. 58.

C. Kellner † has patented the use of chlorine, produced as a by-product at the anode in the manufacture of caustic soda by the electrolytic method, for the purpose of chlorinating all kinds of raw fibres for the preparation of pure cellulose.

Sir William Mather ‡ has devised an apparatus for carrying out all the operations connected with the manufacture of cellulose pulps by the chlorination process, in a continuous manner,

* English patent 938, 1880.
† English patent 24542, 1902.
‡ English patent 8690, 1905.

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without handling the material during the intermediate treatments. The method is based on the circulation principle which has proved so successful in the Mather boiling and bleaching kiers. The raw fibrous material, suitably broken, is packed into travelling vehicles which are divided up into cells of a convenient size, by vertical perforated partitions. The vehicles are then connected up with pipes supplying boiling alkali, hot or cold water, air, chlorine gas or other reagent, and the liquid or gaseous agent is circulated through the mass in a vertical direction by means of an external pump for a suitable length of time, the direction of the current being reversed occasionally. With a series of vehicles arranged on the 'battery' system, the exhaustion of the chemicals can be made complete.

Owing to the fact that a considerable proportion of the pulp obtained from straw consists of cellular tissue (see Fig. 13, p. 109), which, although cellulose, is devoid of fibrous structure, paper made from straw only is found to be much weaker than that made from fibres such as esparto. On the other hand, being a cheap material, and one capable of yielding a very white pulp with a moderate quantity of bleach, it is held in considerable repute by many paper-makers, especially as a material for mixing with esparto. It is sometimes mixed with cotton and linen rags, even in the finest qualities of paper.

Straw cellulose is distinguished by its capacity for hydration and partial gelatinisation under the action of 'beating.' As a consequence, it adds the quality of 'wetness' to the pulp, which again confers the quality of hardness and 'rattle' upon the finished paper.

Wood [Wood cellulose, or 'chemical wood pulp'].—The treatments of the wood by the alkaline processes are comparatively simple operations. Owing to the powerful and general action of caustic soda the hard material requires no special treatment for removing such more resistant structures as knots, or again, rotten wood, both of which survive the bisulphite processes more or less unattacked. The bark is stripped and the wood chipped and passed through a mechanical 'duster' to

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the boiler or digester. These are of the ordinary types: the horizontal cylindrical, or the spherical rotary; or the upright digester. The lye used, in the case of caustic soda, contains 6–8 p.ct. NaOH. After introducing the lye and closing the boiler, the heating is rapidly taken to the maximum steam pressure (90–110 lb.), at which it is maintained for 8–10 hours. The resulting pulp is washed by the process of economic lixiviation in successive tanks, and is obtained of a brownish-grey colour. The dark brown lye is treated for the recovery of the soda by the process of evaporating and calcining.

Sulphate or Sulphide Process.—In this variation of the soda process advantage is taken of the fact that sulphate of soda is reduced to sulphide in the process of evaporating and igniting with the organic matter dissolved from the lignocellulose. In the first instance caustic soda must be added with the sulphate. After boiling with a lye containing 3 parts of the latter to 1 part caustic, evaporating and igniting, an ash is obtained with about 80 p.ct. Na_2O in the form of carbonate, hydrate and sulphide. For a subsequent operation sulphate is added to the amount of about one-third of the total soda compounds, and in a succession of operations the soda lost is made up by additions of sulphate.

The main objection to this process (which is not practised in England) is the formation of organic sulphur compounds of penetrating and objectionable smell. It yields a pulp of excellent quality, for which the coniferous woods are exclusively used as raw materials.

The Sulphite Process.—The introduction and development of this process to its present position of first rate importance marks an epoch in paper-making. As the alkali processes of treating esparto, etc., mark the period 1850–75, the 'bisulphite wood' industry is a main feature of the period 1875–1900: both adding to the paper-maker's supplies, celluloses of different characteristics from the 'rag' celluloses, chemically inferior, but structurally offering certain advantages in regard to the production of cheap papers.

As already explained, these processes rest primarily on the

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action of sulphurous acid, which fact was certainly recognised by B. C. Tilghmann, the original inventor of these processes.* At that period, however, the practical manipulation of sulphurous acid of the requisite concentration in aqueous solution (8–12 p.c. SO_2) was a problem yet to be solved. Hence it was that the alternative of the bisulphites was fixed upon by the pioneer inventors named in the historical summary of p. 69; and these processes have, in fact, been developed, to the entire exclusion of the chemically simpler process in which the pure acid is used. This latter process, though practically demonstrated by Prof. Pictet in 1883–86 as having some important advantages, has not been industrially developed.†

In the development of the bisulphite system, the work of Ekman and his associates in the period 1870–80 certainly takes first rank. The later work of Mitscherlich in Germany and Partington in this country contributed largely to the establishment of the industry upon its present colossal scale. It is not, however, within the scope of this work to follow the history of this process in detail. The achievements of successive inventors have been in the perfection of the chemical engineering of the process; whereas its essential features and the character of the pulp have remained very much as they were established twenty years ago.

We may briefly notice some of the more important technical difficulties, the overcoming of which, with the various ways of doing so, really constitutes the history of the development of the manufacture.

Preparation of Bisulphite Liquor.—In practice the bisulphites of lime and magnesia are exclusively used. The source of the sulphur dioxide is sulphur or pyrites. Sulphur 'burning'—the union of sulphur with atmospheric oxygen, according to the simple equation $S + O_2 = SO_2$—is a reaction requiring careful regulation. To supply 1 lb. of oxygen for the combus-

* U.S. Patents 70,485, 1867, and 92,229, 1869.

† For further information we may refer the reader to a brochure by the authors: 'The Pictet-Brelaz System of preparing Wood Cellulose.' London, 1887. E. & F. N. Spon.

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tion of 1 lb. of sulphur, the quantity of air required is 54 cubic feet. Excess of oxygen leads to waste in two directions: the surphurous acid is further oxidised to SO_3, and the temperature of combustion is increased to the point of volatilisation of sulphur.

In absorbing the gas two methods are employed: (*a*) the basic substance in the form of oxide is prepared in a state of fine division and suspension in water, and the sulphur dioxide (diluted with nitrogen) is caused to pass through the liquid mixture; (*b*) the basic substance in the form of carbonate is presented in large masses to the action of the gas, with a regulated stream of water flowing in the opposite direction.

For each of these typical methods a large number of different forms of apparatus have been devised, the common aim being the continuous and automatic production of a liquor of the requisite concentration (total SO_2 p.ct.), and composition (ratio of free SO_2 to SO_2 combined with CaO and MgO) with the minimum waste of SO_2 escaping unabsorbed, and the minimum incidental oxidation to sulphuric acid.

The following is given by Griffin and Little* as the composition of a standard bisulphite liquor prepared from dolomite;—

SPECIFIC GRAVITY AT 15°, 1·0582.

	Per Cent.			
SO_2 Sulphurous acid.	4·41	combined as	Sulphate of lime	0·22
SO_3 Sulphuric acid	0·13		Bisulphite of lime	2·84
CaO Lime	0·95		Bisulphite of magnesia	3·04
MgO Magnesia	0·72		Free sulphurous acid	0·11
SiO_2 Silica	0·02			

Preparation of the Wood.—Unlike the alkali process, which resolves all the compound celluloses, the bisulphite treatment is a specific resolution of the ligno-celluloses; and to attack these uniformly and normally the wood must be freely and rapidly penetrated by the solution. Hence, first, the bark must be completely removed, and the knots of the wood must be dealt with, either by boring out previously to the digestion, or by removal after the boiling.

* 'Chemistry of Paper-Making.'

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In addition therefore to breaking up the mass of the wood mechanically (1) by chipping, and (2) by further disintegrating the chips by means of crushing rolls, a careful sorting out of rotten knots and unsound portions precedes the transference to the digesters.

The Digesters.—Apart from variations in form as between cylindrical and spherical rotary boilers, and the stationary upright digester, the problem of a satisfactory acid-resisting material or lining for the interior of the boilers has been more or less perfectly solved by a large number of inventors. At the outset, lead linings were exclusively used. This metal, in union with an iron shell, involves the effects of the unequal expansion of the two metals under heat, with the result of a 'creeping' of the lining. To minimise this defect, and at the same time to provide adequate support for the 'soft' and heavy metal, many types of construction have been devised. While, however, in the process of evolution a very satisfactory control of these numerous difficulties was arrived at, the lead linings have at this date given way to non-metallic protective coatings, composed of 'cements' of varying composition, and variously applied. The introduction of these linings appears to date from the observations of Brungger in 1883, that an iron pipe temporarily used for the steam supply to a digester was rapidly coated with a protective scale derived from the bisulphite liquor. Proceeding from this observation, it was found in effect that a plain iron digester could be provided with such a protective coating by introducing the ordinary bisulphite liquor into the digester, previously heated by the steam jacket to 110° C. The method was successfully practised for some time, but has again given place to linings of ordinary cement, e.g. a mixture of Portland cement and silicate of soda (Wengel), ground slate and silicate of soda, a mixture of ground slate or glass and Portland cement (Kellner). In other developments a lining of Portland cement is faced with special bricks or tiles, or even slabs of tempered glass.

Boiling Process.—The conditions and duration of the digestion vary somewhat in the different systems of treatment.

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As an average, about 16–20 hours is required at a pressure of 75 lbs. On the Mitscherlich system a maximum pressure of 45 lbs. obtains, and the time required is much longer, viz. from 70–80 hours. During the process the excess of pressure is relieved from time to time by blowing off, and the sulphurous acid thus escaping is led to one of the 'reaction towers,' in which it is again combined with basic oxides to form fresh liquor.

The Products are the pulp, or fibre, and the waste liquor containing the sulphonated lignone bisulphite compounds.

The unbleached fibre, in its washed condition, is still of course an impure cellulose. The following typical analyses are given by Griffin and Little * in illustration of variations in the ordinary market varieties.

—	Mitscherlich Process. Slow Digestion.	Rapid Digestion.			
Moisture	9·000	6·15	6·70	6·57	6·45
Organic matter soluble in dilute acid	0·516	..	..	..	..
Organic matter soluble in dilute alkali.	1·505	2·53	2·26	4·25	1·52
Resin	0·060	..	..	..	..
Cellulose	80·800	85·33	89·74	88·12	81·51
Mineral matter (ash)	1·500	1·00	0·45	0·33	0·65
Lignone (by difference)	6·619	5·01	0·85	0·73	9·87
	100·000				

It appears therefore that the better grades of sulphite pulp or half-stuff yield from 85 to 90 p.ct. of 'pure,' i.e. bleached cellulose, each calculated to the same basis of 'air-dry moisture.'

The waste liquor contains the sulphonated lignone compounds, the composition of which we have dealt with on p. 68. The problem of utilising these by-products was investigated by the authors in 1883–5. It was found that they are largely

* Loc. cit., pp. 267–8.

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precipitated by gelatin in presence of sulphuric acid or alum, the precipitate agglomerating to a caoutchouc-like mass of greyish colour. The compound thus obtained is soluble in weak alkaline solutions—e.g. solutions of sodium sulphite, phosphate, carbonate—and in this form is available as a sizing material. *

The preparation of the material has been further developed in recent years by Mitscherlich. † In engine-sizing paper (see p. 209), the solution is added to the beaker, and the colloidal compound is thrown out of solution by the addition of a calculated proportion of sulphate of alumina. It contributes in this way to the welding together of the fibres in the machine, i.e. to the 'closing' and toughening of the sheet.

Recent investigations by H. Seidl ‡ have confirmed those of Tollens and of the authors as to the composition and constitution of the dissolved lignone derivatives, and have also resulted in another practical application of these waste liquors, viz. to replace tartar and lactic acid as adjuncts to the process of mordanting wool with soluble chromates. §

Such uses, however, for a by-product produced on an enormous scale, must be regarded as of relatively small importance; and in fact are hardly sufficient to affect their present position as 'waste products'—from which it remains for future researches to rescue them.

Jute, Flax and Hemp, Scutching Waste, Manila, etc.—In addition to the processes above described, all of which are concerned with the production of pure celluloses of the respective classes, and for use in writing and printing papers, a number of raw materials are treated by less severe methods, producing a purified and disintegrated form of the original raw material, and by no means a pure cellulose. Pulps of this sort are used for the most part in wrapping papers.

The boiling processes already described under Esparto and

* English Patent 1548, 1883.
† German Patent 82,498, 1893.
‡ Rev. Gen. d. Mat. Col. 1898, pp. 370–3.
§ See also Journ. Soc. Chem. Ind. 1898, pp. 923 and 1043; English Patent 19,005, 1897.

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Straw are, with certain modifications, equally applicable to fibres of this class. For convenience in manipulation they are usually cut into small pieces by a machine such as is shown in Fig. 18, and are then cleaned and dusted in a willowing machine. The boiling process calls for no special notice beyond what has been already said with regard to other fibres.

A cheaper method, and one which is largely adopted in mills which make wrapping and packing papers, consists in boiling the jute or other fibre with lime. Such a treatment is usually not so effective as one in which caustic soda is used, and the fibre produced is harder and coarser in every way. The yield of pulp, however, owing to the fact that the fibre is imperfectly resolved, is greater. In other cases also, as a matter of economy, lime may be advantageously employed.

Jute and Adansonia are largely used for papers where strength is of more importance than appearance, such, for example, as paper for telegram forms, strong wrapping paper, etc.

Jute.—In the form of cuttings or 'butts,' spinners' wastes and bagging—is usually boiled with lime in cylindrical or spherical rotary digesters. By the use of this base at comparatively low boiling pressures (10–20 lbs.) a well-softened half-stuff is obtained, which yields easily to the action of the beaters.

It should be noted, on the other hand, that jute may be fully resolved to a cellulose of very valuable paper-making quality. In this case the treatment required is either (1) a severe treatment with caustic soda, as for the woods, but at somewhat lower pressures (70–90 lbs.) and with less alkali proportioned to its lower percentage of lignone groups; or (2) a relatively light alkaline treatment followed by treatment with chlorine gas and subsequent removal of the products of chlorination by solution in alkaline liquids.

Flax and Hemp Wastes.—In the mechanical processes of separating the flax and hemp fibres, a fibrous waste is produced consisting of the bast fibres themselves, with varying proportions of the wood of the stems. These and the lower grades of spinners' wastes are usually worked up by the paper-

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maker, *not* for a pure cellulose, but for a half-stuff of less purity and therefore low colour. Various methods of alkaline treatment are adopted, i.e. boiling under pressure with lime or soda, or mixtures of the alkalis. In certain mills the method of chlorination has been practised for the purpose of attacking and resolving the wood. In this case as in that of jute, the preliminary alkaline treatment may be 'milder.'

Attention may be called to the industrial problem of working up for paper-making half-stuff the enormous quantities of flax 'straw' which are wasted, in fact burned, in countries where the plant is grown for seed (linseed) only, as in the western states of North America. After separating the seed by thrashing, the 'straw' is not in a condition for treating for a textile fibre. It contains, however, 20–25 p.ct. of such fibre, and by a treatment severe enough to break down (chemically) the wood and the cuticular celluloses, a 'cellulose' half-stuff is obtained which undoubtedly ranks very high as a paper-making material. The utilisation of flax in this way is again the subject of serious industrial enterprise, and it would appear that the product is destined to become an important staple.

Manila may be taken as the representative of the rope-making fibres, in which group are included the various aloe fibres (Sisal, etc.) and Phormium. The paper-making qualities of manila are sufficiently characteristic to yield papers easily identified by their toughened and parchment-like quality. The fibre comes to the mill chiefly in the form of old ropes. These are cut down by hand and subsequently further disintegrated in machines, in which the material is cleansed by dusting. It is then boiled with soda or lime under a varying change of conditions, according as it is required for envelope papers, cartridges, or brown wrappings.

Miscellaneous Raw Materials.—In addition to the staple raw materials which are treated chemically in the paper-mill as above described, there are a large number of fibrous products which fulfil in themselves the requirements of the paper-maker, but which from various causes, such as cost of collecting or transport, are not generally available.

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Bamboo.—The numerous species of *Bambusa* furnish a stem which may be broadly characterised as a gigantic straw, and, when resolved by a severe alkaline treatment, yields a pulp which has very much in common with the celluloses of our cereal straws. This raw material was thoroughly investigated by Thomas Routledge in the period 1870–5, and many attempts have been made to take advantage permanently of its proved capacities, but the matter remains practically undeveloped.

Mégasse is the name given to the fibrous tissue of the sugar-cane after the extraction of the juice—this cane or stem having a close resemblance to the bamboo. The material has been successfully treated, but the yield of pulp is low, and it is available only for the lowest class of papers.

Adansonia is the fibrous bast or inner bark of the *Adansonia digitata*, a tropical species which grows luxuriantly in the West African forests. It finds a limited use in this country, especially for wrapping papers requiring a very high finish. For this purpose it is boiled with lime. Treated with soda, it may be fully bleached to a cellulose of very valuable paper-making quality.

Sunn Hemp (*Crotalaria juncea*).—This is a useful fibre, and it finds a limited sale in the English market. It is a bast fibre separated from the stem of the plant after a retting process. It has been tested experimentally for paper-making, and for papers of the higher grades, but it has not come into general use.

Rhea, Ramie, China Grass.—These are bast fibres of species of the nettle order. They readily yield, under alkaline treatment (caustic soda), a pure cellulose, and the ultimate fibres are distinguished for their exceptional length. The fibre comes to the paper-maker in the form of spinners' wastes, and is available for papers of the highest grades. It is used to a limited extent for papers of special quality.

'Broke' Paper.—Under this head may be included all the partially formed paper which is always obtained in greater or less degree when a paper-machine is started, or such portions as are occasionally unavoidably damaged in its passage over the

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drying cylinders, together with the imperfect or rejected portions. It may also include used or waste paper, a large proportion of which, if not too dirty, is remade into paper. The cleaner portions, especially if they have not been dried, are frequently returned direct to the beaters, and mixed with other pulp. That which has been actually made into paper requires to be softened by boiling in water and gentle breaking in an engine. It may be necessary to heat it for a short time in a weak solution of caustic soda. This may be done either in a breaker or in special tanks provided for the purpose. Paper which has been printed upon requires a rather more drastic treatment, and it must of course be used for an inferior quality

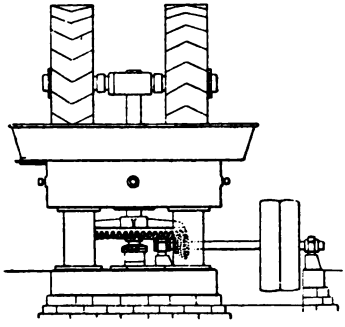

FIG. 27.

of paper, as it is impossible to get it to as good a colour as the original pulp from which it was made—at least not economically. 'Broke' paper may be advantageously disintegrated by means of an edge-runner. It consists of a pair of stones arranged in the same way as an ordinary mortar-mill (Fig. 27).

Under the crushing and milling action of the stones, the fibres of the broken paper are not only separated, but are also further reduced and disintegrated, thereby imparting a 'wetness' to the pulps with which they are mixed. For certain purposes this action of the edge-runners is positively advantageous, but in other cases it may be desirable to maintain the length of the fibres and the 'freeness' of the pulp unimpaired. In

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such cases a pulping or kneading machine, such as Würster's or Dietrich's, may be substituted for the edge-runners. These machines, besides yielding the fibres in an unmodified condition, also consume far less power in comparison with their out-put than the edge-runners. The Würster pulping machine is illustrated in Fig. 28. The dry sheets of paper are fed into the hopper at one end together with sufficient water and the pulp issues continuously at the other end. Hard, tub-sized papers and imitation parchment papers, however, require to be softened by boiling with water before treatment in the kneading machine. Kneading machines are likewise useful for pulping up sheets of mechanical or chemical wood pulps preparatory to charging the beaters.

Würster's machine, as at first introduced, consisted of two horizontal arms provided with teeth revolving in opposite directions. The paper, together with water and steam, is admitted, through a hopper at one end and discharged through an outlet at the other. To create sufficient back pressure to ensure thorough disintegration, the outlet can be regulated in size by the adjustment of a damper. The shape and arrangement of the prongs is now varied to suit special requirements.

Another machine also employed for the same purpose is the Cornet Cone Breaker, consisting of a solid cone revolving inside a fixed cone both provided with prongs. At one end is a hopper into which the shavings softened by water and steam are forced, at the other end the pulped material is discharged.

Mechanical Wood Pulp.—A very large quantity of pulp used in the commoner kinds of paper, such as cheap news, etc., is obtained by disintegrating wood by mechanical means alone, no chemicals being employed. The idea of making paper in this way dates back about 100 years, but owing to the want of suitable machinery it is only lately that a good product has been obtained. The following are, in a general way, the details of the process employed :—

The wood is first cut up into blocks, the size of which is determined by the width of the stones used for grinding ; any

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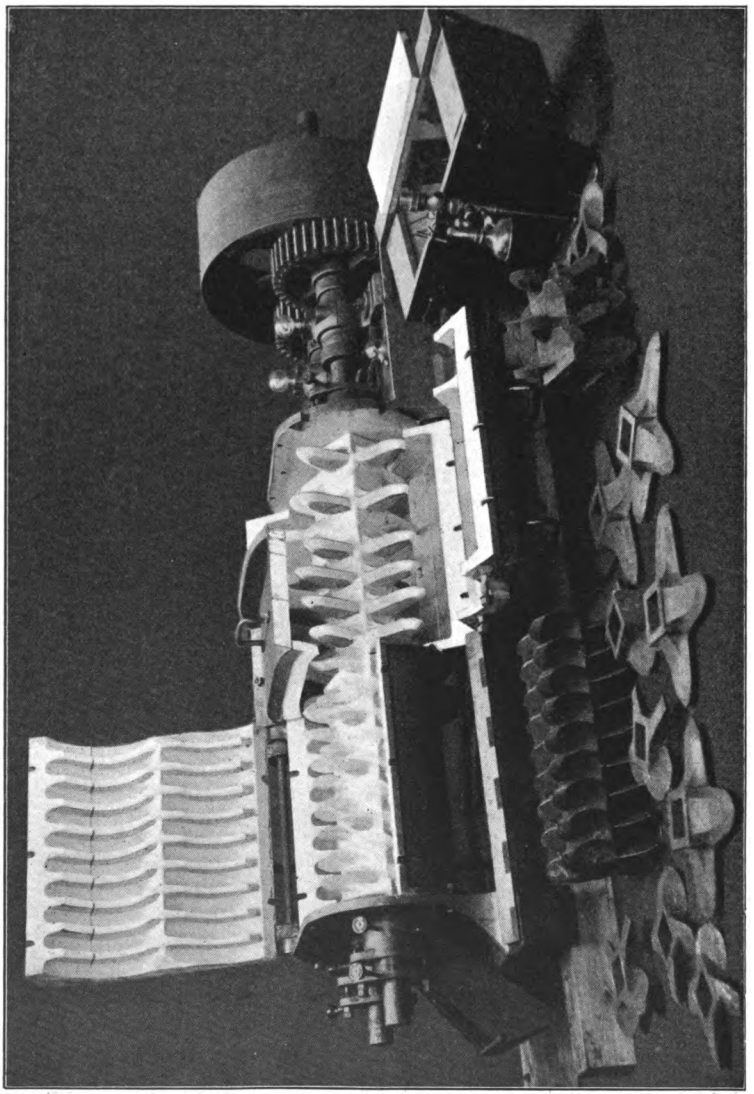

FIG. 28.

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knots present are cut out with an axe. The stones are made of sandstone, and are covered over three quadrants with an iron casing, the remaining quadrant being exposed. The surfaces of the stones are made rough by the pressure of a steel roll studded with points, and which is pressed against it while revolving. In addition to this, channels about ¼ in. deep are cut into the stone at distances of 2–3 in. They are made in two sets, crossing each other in the centre of the stone, and serve to carry off the pulp to the sides of the stone, in addition to giving increased grinding surface. The pressure of the blocks of wood against the stones is steadily maintained by screws worked by suitable gearing; this is necessary in order to obtain a pulp of uniform character. A stream of water is kept constantly playing on the stone; by this means the pulp, as fast as it is formed, can be conveniently carried away. It is first passed through a rake, which retains small pieces of wood that have escaped grinding. The stream of pulp then passes through the sorters, the object of which is to keep back such portions of the wood as have not been sufficiently disintegrated. These consist of cylinders about 3 ft. long and 2 ft. in diameter, covered with a coarse wire-cloth. The fibres that are retained by this wire fall into the refiners, which consist of a couple of horizontal cylinders of sandstone, the upper one only of which revolves. Here they are further disintegrated, and are again passed through the wire-cloth; this is repeated until all the fibres have passed through. The pulp, after passing through the first sorter, may be conducted through a series of gradually increasing fineness, and, by this means, be separated into different qualities. Though pulp so prepared cannot compare with chemically-prepared stuff, as the fibres are extremely short and have comparatively little felting-power, it may be used with advantage as a sort of filling material.

In some machines the grinding stones are mounted vertically on horizontal shafts, whilst in others they are mounted horizontally on vertical shafts (Fig. 29). The former type appears to have gained the preference in America, whilst the latter type seems to preponderate in Europe.

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Two kinds of mechanical wood pulp can be prepared, according as the wood is ground across the grain or in the direction of the grain. The cross-grain fibres are shorter and more mutilated than the long-grain fibres, but the latter do not give

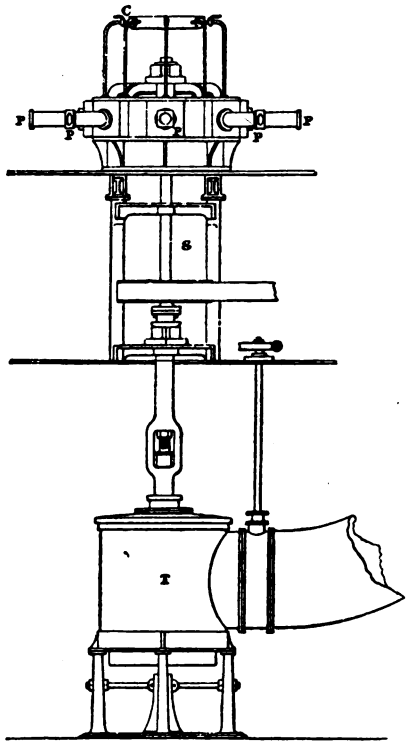

FIG. 29.

so fine a pulp. The process of long-grain grinding is not, however, very much used.

Grinding machines have been constructed in which the flat surfaces of the stone are employed instead of the periphery (Figs. 30 and 31). In such machines the different parts of

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the wood-blocks are ground at different speeds, and the pulp produced is a mixture of cross-grain and long-grain fibres, the relative proportions of which may be varied at will.

Various modifications of the foregoing process have from

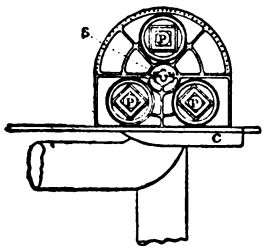

FIG. 30.

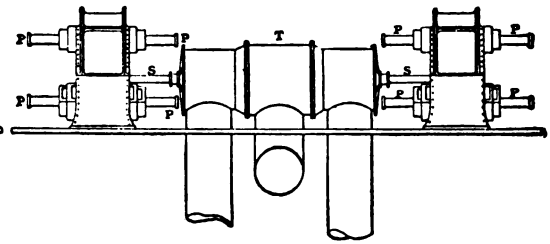

FIG. 31.

time to time been proposed. Among others, that of softening the wood by previous soaking in water, or steaming, proves to be valuable, as by so doing it is found that a longer fibre can be obtained, the soft wood being more readily torn away by the stones. Some inventors have proposed to replace the sandstone by an artificial stone containing a large quantity of emery.

At the present time two main varieties of mechanical wood pulp are prepared, viz., 'cold-ground' and 'hot-ground.' Cold grinding is effected under moderate pressures between wood and stone, the pulp being washed away by copious streams of water. In hot grinding the pressure of the wood against the stone is extremely high and the stream of water reduced to a minimum, so that a very high temperature is developed at the surface of contact. Hot grinding is more economical than cold grinding, and is stated to yield a finer and longer pulp than cold grinding, but cold-ground pulp possesses a quality known to the paper-maker as 'wetness' or hydration in a higher degree.

An improved method of preparing mechanical wood pulp lately patented by Mr. A. L. Thune, of Christiania, has been communicated to us by Mr. Carl Christensen.

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The apparatus employed is shown in Figs. 29, 30, and 31. Fig. 29 illustrates an arrangement of grinding apparatus fixed direct on to a turbine. The stone is fastened on to the shaft S worked by the turbine T. The wood in the form of small blocks is kept in contact with the stone by a number of hydraulic presses P.

A somewhat similar arrangement, but placed horizontally, is shown in front and side elevations in Figs. 30 and 31. The same letters correspond.

The ground and sorted pulp is made into thick sheets by means of the board machine shown in Fig. 32. The pulp mixed with water passes down the shoot D into the vat B in

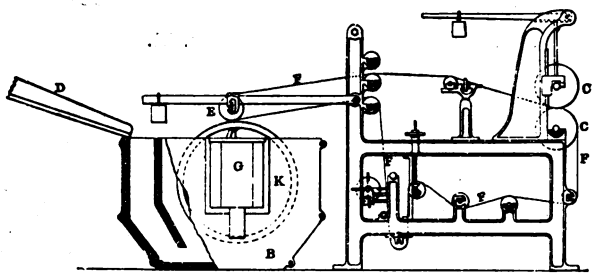

FIG. 32.

which the cylinder K revolves. This cylinder is covered with wire-cloth, and as it revolves it takes with it a certain quantity of pulp in the form of a continuous sheet. This sheet is taken on to the endless travelling felt F by the small couch roll E. When it reaches the rolls CC it is wound round the upper one, from which it is removed when a sufficient thickness is obtained. Obtained in this form the pulp is readily transported.

The woods commonly employed are white pine, spruce and aspen. The last-named yields a pulp of a better colour, but of inferior strength.

Paper containing mechanical wood pulp is very liable to become discoloured by the action of air and light, the ligno-celluloses being much more readily acted upon than the

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TABLE OF STRENGTH OF CAUSTIC SODA SOLUTIONS (15° C. = 59° F.) (TÜNNERMAN).

Specific Gravity.	Degrees Twaddell.*	Per Cent. Na_2O.	Equivalent Percentage of NaOH Caustic Soda.
1·0040	0·80	0·302	0·389
1·0081	1·62	0·601	0·778
1·0163	3·26	1·209	1·560
1·0246	4·92	1·813	2·339
1·0330	6·60	2·418	3·120
1·0414	8·28	3·022	3·900
1·0500	10·00	3·626	4·678
1·0587	11·74	4·231	5·459
1·0675	13·50	4·835	6·238
1·0764	15·28	5·440	7·019
1·0855	17·10	6·044	7·798
1·0948	18·96	6·648	8·578
1·1042	20·84	7·253	9·358
1·1137	22·74	7·857	10·138
1·1233	24·66	8·462	10·919
1·1330	26·60	9·066	11·698
1·1428	28·56	9·670	12·477
1·1528	30·56	10·275	13·258
1·1630	32·60	10·879	14·037
1·1734	34·68	11·484	14·818
1·1841	36·82	12·088	15·597
1·1948	38·96	12·692	16·374
1·2058	41·16	13·297	17·157
1·2178	43·56	13·901	17·937
1·2280	45·60	14·506	18·717
1·2392	47·84	15·110	19·497

NOTE.—It must be borne in mind that the above numbers refer only to solutions of pure caustic soda. With liquors containing sodium chloride, sulphate, etc., the specific gravity will give an erroneous view of the amount of alkali present, as these salts of course raise the gravity. For example, a liquor prepared by causticising a solution of recovered soda has a specific gravity of 1·05 (10° Tw.). According to the above table, this corresponds to 6·043 per cent of 60 per cent. caustic. Tested by means of standard acid it showed 4·520 per cent. Too much reliance should therefore not be placed upon determinations of specific gravity, but in important cases the actual amount of alkali should be determined by titration with standard acid.

* Each 1° Tw. represents 0·005 units of 'gravity,' therefore, to convert degrees Twaddell into specific gravity, multiply by 5, add 1000, and divide by 1000.

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celluloses isolated from them. Such fibre is, moreover, of low felting quality; it has, in fact, little to recommend it but its comparative cheapness. It is nevertheless used in large quantities, some cheap papers being made almost entirely from it.

In reference to the alkaline treatment of fibres dealt with in the early part of this chapter, a Table of Strength of Caustic Soda Solution will be found useful for reference, for which see the preceding page.

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CHAPTER VI.

BLEACHING.

THE bleaching of the pulp or half-stuff resulting from the chemical treatment of the various raw materials, is the second stage in the purification of the cellulose or compound cellulose; in the former case the residues of non-cellulose constituents are entirely removed, in the latter the product is more or less 'whitened,' but a considerable proportion of the non-cellulose constituents survive the process and consequently the pulp remains coloured more or less. The 'chemical' wood-pulps, it may be mentioned, are largely used in the unbleached condition; the 'sulphite' pulps are usually of a pinkish-grey colour, and they are used directly in 'toned' or greyish-white papers. The 'mechanical' wood pulps, for reasons which will appear, are used almost universally without any bleaching treatment, and they give a greyish tone to the lowest grades of 'printings,' of which they are the main constituent.

Paper-makers' bleaches are essentially processes of oxidation. The agents employed are alkaline compounds of certain acid, oxidising oxides, and the alkalis contribute to the effect by hydrolysing the coloured compounds present in the fibre to be bleached, and by combining with the colourless products of the oxidation. Though several oxidising or bleaching agents are available, the use of 'bleaching powder' so enormously preponderates, that it is the only method we need consider in any detail. Bleaching powder, commonly known as 'chloride of lime,' is prepared by the action of chlorine gas upon slaked lime, the later absorbing more than half its weight of the gas. The

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resulting compound is usually formulated as $Ca\begin{matrix}OCl\\Cl\end{matrix}$; but when treated with water the compound is hydrolysed and resolved into equal molecules of calcium chloride, $CaCl_2$, and *Calcium Hypochlorite*, $Ca(OCl)_2$, the latter being the active oxidising or bleaching compound. The hypochlorites are the salts of the acid HClO, which is the hydrate of the oxide Cl_2O, thus :—

$$Cl_2O + H_2O = 2HClO.$$

It must be noted also that the resulting hypochlorous acid decomposes, in acting as an oxidant, into HCl + O, and therefore the oxide Cl_2O is equivalent in oxidising action to O_2, and *vice versa*, the O_2 obtained from bleaching powder represents $2Cl_2$, and as the active constituent of these bleaching solutions is always expressed in terms of *Chlorine*, it is now clear that the apparent loss of half the active chlorine, as the inert $CaCl_2$, which attends the act of solution in water, is only a change of terms, viz. to oxygen. In this sense, therefore, and in regard to oxidising actions, the whole of the chlorine of a normal bleaching powder is 'available chlorine.'

For the actual composition of a normal bleaching powder we cite an analysis by Griffin and Little*:—

Available chlorine	37·00	Total Cl 37·60
Chlorine as chloride	0·35	
Chlorine as chlorate	0·25	
Lime	44·49	
Magnesia	0·40	
Silicious matter	0·40	
Oxides of iron, alumina and manganese	0·48	
Carbonic acid	0·18	
Water and loss	16·45	
	100·00	

This analysis is one of a series, the purpose of which was to determine the rate of depreciation of bleaching powder when stored in the usual hard wood casks at temperatures not exceed-

* 'Chemistry of Paper-Making,' p. 278.

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ing 62° F. At the expiration of eleven months the 'chlorine' numbers of the above had changed to—

Available chlorine	33·80
Chlorine as chloride	2·44
Chlorine as chlorate	0·00

During the same period the carbonic acid had increased from 0·18–0·80.

It is to be remembered, therefore, that bleaching powder is an unstable compound, and the supplies should be stored in dry, cool places, and out of the range of any possible contact with products of combustion, i.e. of coal or coal-gas.

Preparation of the Solution.—The solution is best prepared in a vessel provided with stirrers or agitators, whereby a thorough mixture of the bleaching powder and water is obtained. Bleaching powder always contains a certain amount of free lime and calcium carbonate, which remain undissolved as a residue which should be allowed to settle to the bottom of the vessel, and the clear liquor run off. The residue may then be again treated with water, or with dilute liquor obtained in a previous operation too weak to be conveniently used for bleaching; such liquors may be stored in a separate tank and used for dissolving fresh powder. In this way a strong stock solution can be economically prepared, the powder being thoroughly exhausted. The washing should be repeated as frequently as possible, after which the residue may be allowed to drain. This operation is best conducted on a filter-bed provided with an air-pump similar to that described in Chapter XI. The residue is obtained in this way as a hard cake, containing about 60 p.ct. of water. If the above operations have been properly conducted, it should not contain more than about 0·25 p.ct. of chlorine. It is, as above stated, mainly composed of lime, i.e. the hydrated oxide of calcium $Ca(OH)_2$, and carbonate of lime. Calculated on the dry substance, the former amounts to about 60 p.ct. and the latter to 30 p.ct.

The original powder should contain from 33·0 to 37·0 p.ct. of 'available chlorine,' that is, chlorine which is effective in the bleaching process.

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If possible, one or more large store tanks should be provided for the strong bleach liquor, so that time may be given for the complete separation of the insoluble portions. The liquor can be drawn off with a 'siphon' pipe without disturbing the residue.

It is generally advisable that only clear liquor be used, as a milky solution of calcium hypochlorite is much more sluggish in its action than one which is perfectly clear and bright.

A convenient strength for the stock solution is 6° Twaddell: this corresponds to about half a pound of bleaching powder to the gallon.

The solution of the hypochlorite is also liable to deterioration with loss of 'chlorine' strength. It must, therefore, be stored in cool places, and there should be a minimum of exposure to the atmosphere. This is secured by storing in relatively deep vessels.

The following table compiled by Lunge and Bachofen, shows the concentration of 'active chlorine' in freshly prepared solutions of bleaching powder at various specific gravities.

Sp. gr. at 15° C.	Grms. per litre Active Chlorine.	Sp. gr. at 15° C.	Grms. per litre Active Chlorine.
1·1000	61·50	1·0450	26·62
1·0950	58·00	1·0400	23·75
1·0900	55·18	1·0350	20·44
1·0850	52·27	1·0303	17·36
1·0800	49·96	1·0250	14·47
1·0750	45·70	1·0200	11·41
1·0700	42·31	1·0150	8·48
1·0650	39·10	1·0100	5·58
1·0600	35·81	1·0050	2·71
1·0550	32·68	1·0025	1·40
1·0500	29·60	1·0000	Trace

The following reactions of the hypochlorites and their practical bearings are important:—

1. They liberate iodine from the iodides. Free iodine gives a deep indigo blue colouration with starch. Hence the usual test solution for the presence of these compounds, viz. a starch paste containing potassium iodide.

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Test Papers are made by soaking pure cellulose (filter) papers in the mixture and rapidly drying in a pure atmosphere. Care must be taken to avoid oxidation of the iodide to iodate, as a mixture of these salts is decomposed by the weakest acids with liberation of iodine, thus—

$$5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2.$$

In using the test papers with acid solutions the test papers should be themselves tested with a weak acid (acetic).

2. In adding the hypochlorites to a soluble iodide in presence of acid, the following reaction takes place :—

$$Cl_2O = 2HClO + 4HI = 2HCl + 2H_2O + 2I_2.$$

In this case both the chlorine and oxygen are converted into the joint equivalent of free halogen. The reaction affords a rapid and satisfactory analytical method, i.e. for estimating 'available Cl.' The iodine liberated is titrated with thiosulphate.

3. The hypochlorites are instantly 'destroyed' by hydrogen peroxide, thus—

$$NaClO + H_2O_2 = NaCl + H_2O + O_2;$$

that is with production of entirely 'neutral' compounds. In estimating the alkalinity or acidity of a bleaching liquor the hypochlorite is destroyed by a neutral solution of the peroxide; after which ordinary indicators may be used, and the products titrated with acid or alkali to the neutral point.

4. The neutral sulphites are oxidised to the neutral sulphates :—

$$Na_2SO_3 + NaClO = Na_2SO_4 + NaCl.$$

Both the above reactions are useful therefore in 'neutralising' or destroying excess of 'bleach.'

5. 'Organic' or carbon compounds react with the hypochlorites in various ways; (*a*) they are simply *oxidised*, thus—

$$\underset{\text{Aldehyde}}{R\cdot COH} + NaClO = \underset{\text{Acid}}{R\cdot COOH} + NaCl.$$

(*b*) they are *chlorinated* in various ways; thus, saturated

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compounds, such as alcohol, acetone, aldehyde, yield *chloroform* (CCl_3H): unsaturated compounds may yield chlorhydrins, $CH_2:CH_2 + ClOH = \begin{matrix} CH_2Cl \\ CH_2OH \end{matrix}$, or if aromatic derivatives, chlorinated phenols, quinones, etc. Also it must be remembered that strong hydrochloric acid liberates *chlorine* from the hypochlorites; a large number of acids set free the hypochlorous acid, which however is very unstable and readily decomposes with liberation of chlorine. Thus the ligno-celluloses are very liable to *chlorination* under treatment with bleaching powder solution, as a result of the secondary reactions. In bleaching jute (half-bleach) or wood pulps (cellulose bleach) a basic reaction should be maintained throughout. The presence of chlorinated lignone compounds is shown by the colour reaction with sodium sulphite (p. 57).

The method of testing the powder and its solution will be described in Chapter XIV.

Bleaching Process.—The bleaching of rag stock may be carried out either on the rags before breaking, or on the 'half-stuff.' In the former case the boiled rags are rinsed until free from alkali, and are then loaded into the bleaching vessels. The treatment is usually carried out in a 'tumbler,' or revolving barrel, made of wood and suitably lined internally with a resistant material. The barrel is charged through a manhole; the liquor is then run in, and the mixture is kept in constant circulation by the rotation of the barrel. In other cases the bleach-liquor may be pumped continuously through the rags contained in a closed stationary vessel, whilst in many mills the rags are merely immersed in the bleaching liquor contained in large stone tanks without any circulation other than that given by the men in attendance.

It is, however, more rational to carry out the bleaching on the 'half-stuff.' The washed and broken pulp is placed in a 'potcher,' together with the necessary quantity of bleach liquor mixed with the minimum quantity of water required to determine the proper circulation of the mass. Very frequently the 'breaker' itself answers the purpose of a 'potcher' also.

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A very good system consists in a preliminary treatment with bleach in the 'potcher,' followed by a prolonged steeping in tanks. According to Menzies' Eng. Pat. 28 of 1902, the pulp mixed with the bleach is maintained under a pressure of air, and is agitated by being discharged from one closed vessel to another by means of compressed air.

The quantity of water should be kept as low as possible, since it is found that by the use of strong solutions less bleaching powder is required than with weak solutions, and the action is more rapid. On the other hand, with very strong solutions the pulp is liable to be injuriously affected.

Whichever system be followed, the paper-maker may choose between two policies: (1) a rapid bleach by the use of a considerable excess of strong bleach liquor, in which case the residual liquors, after the bleaching is finished, are drained off and used again, with the addition of fresh liquor for the next batch of stock; or (2) a very much slower process, using only a little more than the theoretical quantity of bleach liquor, and allowing it gradually to exhaust itself on the pulp, an operation which requires at least 24 hours.

The first method enables a maximum amount of work to be done with minimum accommodation, but the continuous accumulation of exhausted bleach residues is objectionable, and the further oxidation of the soluble organic matters extracted from the pulp causes a consumption of chlorine which is not represented by useful work. The second system, on the other hand, though safer and more economical, involves a provision of tank-space which cannot always be afforded, especially when the number of different grades of pulp to be treated is large.

Straw and esparto pulp are sometimes bleached in large potchers made of brick covered with cement. The circulation of the pulp is produced by the action of paddles made of wood or, preferably, of iron.

Many 'potchers' are provided with steam pipes, whereby the mass of pulp and liquor is heated. This should be done with great care, so as to avoid superheating in any part, as this is certain to cause destruction of the fibre. The better

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plan, where it can be adopted, is to uniformly heat the pulp before running in the bleach.

The time necessary to produce a perfect bleach depends on the nature and condition of the pulp, on the degree of concentration of the liquor, and on the temperature at which the operation is conducted. Some paper-makers prefer to extend the bleaching over a considerable period of time, in spite of the large accommodation which it is necessary to provide. If this method be adopted, especially in the bleaching of straw or esparto pulps in 'potchers,' the action of the paddles or roll should be stopped, otherwise the fibres are liable to felt together in the form of small grains, which sometimes escape the action of the beating roll, and occasionally find their way into the paper, causing an unevenness of surface. By giving longer time to the bleaching there is less risk of damage to the fibre, and consequently a greater yield of bleached pulp.

The action of the bleaching solution should, as far as possible, be confined to the non-cellulose portions of the fibre. A certain action on the cellulose itself invariably takes place, but it should be reduced to a minimum. The action of bleach upon cellulose has been indicated in Chapter I., p. 44. For further information on this subject the reader is referred to the 'Journal of the Society of Chemical Industry,' 1884, April 29 and May 29.

The bleaching action of calcium hypochlorite in the ordinary condition is very sluggish, but it may be assisted and accelerated in certain cases by the addition of sulphuric or hydrochloric acid. These combine with the lime base and liberate hypochlorous acid, which has a more rapid action than its calcium salt. The acid should be used very sparingly and in a highly diluted condition, and it should be added gradually. The diluted acid should be conveyed by a leaden pipe passing down to the floor of the 'potcher' immediately in front of the roll, and perforated at its lower extremity. A small quantity of acid is quite as efficient as a large quantity, since it is continuously regenerated as the hypochlorous acid is decomposed. If the acid be added in too large quantity, or of too great a strength, it sometimes happens that instead of hypochlorous acid, chlorine

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gas is given off, part of which escapes into the air, thus causing loss. Moreover, the chlorine is liable to enter into combination with the fibre-substance, forming the yellow chlorination products described on p. 57.

This liability is greater in the case of highly lignified fibres, such as wood or jute; in these cases, therefore, the use of acids should be avoided. The best plan is to allow the action of the bleach to continue for some time, only adding the acid when it is nearly exhausted. In this way risk of damage to the pulp is avoided.

In bleaching 'half-stuff' from flax waste or new linen pieces, the acid bleach is useful in resolving the residues of ligno-cellulose or 'sheave.' The acid finish to the bleaching operation is particularly useful as a 'sour' in the case of rags and other pulps which have been prepared by an alkaline boil. The alkaline treatment causes an accumulation of basic matter (calcium carbonate) in the pulp, which may have a deleterious effect on the subsequent sizing operations. By means of the 'sour' the pulp is cleared of these basic residues, and its qualities are thereby improved. It should be mentioned, however, that it is of the greatest importance that the excess of acid should be completely removed, without undue delay, by thorough washing of the pulp with water, otherwise the fibre may become tendered' with the production of hydro-cellulose.

Other means of accelerating the action of the bleaching powder have been suggested, such, for example, as the use of bicarbonate of soda, which by double decomposition forms, with the bleaching powder, carbonate of lime and free hypochlorous acid. It is, however, much too expensive an agent.

Very excellent results are sometimes obtained by substituting sodium or magnesium hypochlorite for the calcium compound. This is done by decomposing a solution of bleaching powder with an equivalent quantity of either sodium sulphate or carbonate, or magnesium sulphate. The precipitate of calcium sulphate or carbonate is allowed to settle, and the clear liquor run off. The soda solution is more sluggish in its action than one of calcium hypochlorite, but it is more

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easily controlled, and is less liable to injure any material treated with it. From a comparative study by the authors of the bleaching actions of these three hypochlorites,* it appears that the chemical reactions are simplest in presence of magnesia, this base favouring *oxidation*; with lime as base there is a greater tendency to *chlorination*; soda is intermediate.

In the case of pulps which are very difficult to bleach, the action can be greatly assisted by washing out the products of the bleaching action, treating the pulp for a short time with a weak alkaline solution, again washing, and then repeating the bleaching process. In this way very refractory pulps can easily be bleached. Even an intermediate washing with water is useful. Such refractory pulps are sometimes obtained in the bisulphite-wood process. Griffin and Little † have put on record a careful investigation of such a case, where the difficulty of bleaching was traced to an impurity of an organic sulphur compound. With an intermediate alkaline treatment the usual high colour was obtained.

In most cases, where a fairly good colour has been obtained by the use of bleaching powder alone, the colour is greatly improved by a souring, or treatment with weak hydrochloric acid, or, better still, with solution of sulphurous acid.

Or the bleaching may be conducted in two or more operations with intermediate treatments with acid.

All these modifications, however, are more or less troublesome, and should only be resorted to when the ordinary method fails.

After bleaching, a certain quantity of hypochlorite, i.e. 'active chlorine,' always remains in the pulp. It may be removed in the potcher itself, or when the pulp reaches the beater. In any case, the methods adopted are the same. (See p. 203.)

In some mills it is the practice to free the bleached pulp from the soluble by-products of the bleaching process by pressing the pulp in hydraulic presses, or by draining in vats pro-

* Journ. Soc. Chem. Ind. 1890.

† 'Chemistry of Paper Making,' pp. 287, 288.

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vided with perforated bottoms. Or the pulp may be made to pass through a pulp-saver.

In modern practice the presse-pâte system is more generally adopted: this is, for evident reasons, the most thorough method of finally purifying the cellulose.

Chlorine gas as a bleaching agent has been almost entirely superseded by the more manageable calcium hypochlorite. Its employment is open to the serious objection indicated before, viz. the liability to form difficultly removable chlorine compounds. Its use as a disintegrating agent has already been alluded to (see p. 139).

The introduction of liquefied chlorine, however, reopens the question of the practical application of the halogen itself.*

A process has been suggested and patented (English patent No. 11,333, 1884), by Prof. Lunge, which involves the use of acetic acid. The quantity required is, however, very small, as during the process of bleaching it becomes regenerated. The free lime in the bleaching powder solution may first be nearly neutralised with a cheaper acid, such as hydrochloric or sulphuric, followed then by the addition of the acetic acid. This process, we are informed, gives excellent results with high-class material, such as the best cotton and linen rags; it is, however, not to be recommended for such materials as straw, esparto or wood celluloses, nor for the jute half-bleaches.

For the bleaching of rags the process invented by Thompson (English patent No. 595, 1883) has also proved effective. The method consists in saturating the material with a weak solution of bleaching powder, and then exposing them to the action of carbonic acid gas, alternating the treatment with liquor and gas until the bleaching is complete. In this way the bleaching action is made very rapid and effective.

The amount of bleaching powder necessary to produce a good white colour differs materially with the fibre to be bleached, and of course with the degree of resolution of the fibre-substance in the preliminary treatment with caustic soda.

* For information on this matter see 'Annalen der Chemie,' **259**, p. 100 (R. Kneitsech).

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The following numbers may be taken to be approximations of the amount necessary to bleach well-boiled pulps :—

	Per cent. Powder, calculated on Original Fibre.
Rags	2 to 5
Esparto	7 „ 12
Straw	7 „ 10
Wood	15 „ 20

A well-boiled pulp should contain from 90 to 95 p.ct. of cellulose, that is, in other words, will lose from 5 to 10 p.ct. in weight in the process of bleaching.

Electrolytic Bleaching.—Various attempts have from time to time been made to bleach by means of electricity—that is to say, by means of the products of the electrolysis of solutions of the chlorides of the alkalis or alkaline earths. The first process to be industrially developed was that of E. Hermite. This process is based upon the electrolysis of a solution of magnesium chloride, this salt having been found to give the most economical results. The solution, at a strength of about 2·5 p.ct. of the anhydrous salt ($MgCl_2$), is electrolysed until it contains the equivalent of about 3·0 grms. chlorine per litre. This solution is then run into the 'potcher' containing the pulp to be bleached ; a continuous stream is then kept up, the excess being removed by means of a drum-washer. This excess, which after being in contact with the pulp in the engine is more or less deprived of its bleaching properties, is then returned to the electrolysing vat, where it is again brought up to the normal strength.

The electrolysing vat consists of a rectangular vessel of slate or other suitable material. The negative electrode may be constructed of zinc ; for the positive it is necessary to employ platinum. Each electrolyser contains a large number of pairs of plates disposed in series, the electrical connection being of course 'in parallel.'

The electrolysed solution has been found to possess very remarkable properties, which have considerable bearing upon the economy of the process. If a solution be taken of equal

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oxidising efficiency with one of calcium hypochlorite, as indicated by the arsenious acid test (see p. 334), it is found that the former possesses greater *bleaching* efficiency than the latter in the proportion of 5 to 3. Moreover, the bleaching is much more rapid, and the loss of weight which the fibre undergoes is less, for equal degrees of whiteness obtained.

It has been shown that by the electrolytic method the bleaching of paper pulp can be effected at much less cost than with bleaching powder. The process has been extensively employed in French mills.

It must be noted here that the 'Hermite' system was originally based upon a continuous circulation of the bleaching liquid in between the potcher and the electrolyser. This, however, is only practicable in the case of rag celluloses; in bleaching esparto and wood the organic matter dissolved in the bleaching liquid leads to many inconveniences, such as frothing, and to a serious loss of current by short-circuiting, and by doing waste work (oxidation) on the dissolved organic matter.

Consequently this and other electrolytic systems have resolved themselves very much into the preparation of a bleaching solution, which is then run into the potcher and used in the same manner as a solution of bleaching powder.

The electrolysers which are most generally used at the present time are Kellner's, in which platinum 'net' electrodes are employed, Siemens-Schuckerts' and Schoop's 'bastard' electrolyser with platinum anodes and carbon cathodes, and Haas and Oettel's, in which both electrodes are made of a graphite composition. In both these apparatus a solution of common salt is converted into sodium hypochlorite; Hermite's magnesium chloride solution appears to be no longer employed. In Haas and Oettel's apparatus the salt solution is kept in continuous circulation by the pressure of the hydrogen evolved during the electrolysis; the solution passes alternately through the cells and through a system of cooling pipes until the desired concentration of 'active' chlorine is obtained.

Although this is a considerable practical simplification, it involves a certain sacrifice of 'bleaching efficiency.' It still

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appears, however, that the electrolytic solutions show a certain economy when compared with solutions of bleaching powder.

According to Haenssermann* 30 parts of electrolytic chlorine in the form of sodium hypochlorite are equivalent in bleaching efficiency to 100 parts of bleaching powder containing 35 p.ct. of 'active' chlorine.

Ahlin states that if the exhausted liquors from electrolytic bleaching be so intimately mixed with air that a milky emulsion is produced, the admixture of this emulsion with the pulp in the 'potcher' in the course of bleaching accelerates the action and increases the whiteness of the product to a remarkable degree.

In estimating the relative costs, the following are the essential data for arriving at the cost of the 'electrolytic chlorine.'

(1) *The unit of current* is the ampère; one ampère in passing through the electrolyte solution liberates its 'equivalent' of 1·3 grm. chlorine per hour at the anode, and the corresponding quantity of sodium at the cathode.

The above are the electro-chemical equivalents, i.e. theoretical numbers; in practice the yield is considerably less than the theoretical, as in this kind of electrolysis there are complications due to secondary reactions.

The current-efficiency decreases very considerably as the concentration of 'active' chlorine increases, and the reaction comes to an equilibrium when the liquid contains about 25 grams of 'active' chlorine per litre. For bleach liquors of moderate strength, containing about 5 grams of 'active' chlorine per litre, the unit of current may be taken as yielding 70–80 per cent. of 'available' or hypochlorite chlorine, say 1 ampère = 1 gram of 'active' chlorine per hour. An interesting discussion of this aspect of the question will be found in the Journ. Soc. Chem. Ind., 1901, pp. 130–132.

(2) The *resistance* against which the current has to be forced varies inversely as the concentration of the salt solution,

* Dingl. Polyt. Journ. **314**.

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and the electrical pressure necessary to force the current against this resistance is measured in units known as *volts*, and a 'pressure' of 3–4 volts is required between the terminals.

The product (ampères × volts = 'watts') is the power consumed, and this may be expressed in the same units as mechanical power, 746 watts being equivalent to one horse-power. Hence we have the following cycle of related quantities :—

About 2 lb. of coal, by combustion under a boiler, are required to produce one horse-power of mechanical energy under economical conditions : this is equivalent to 746 'watt-hours' of electrical energy, but allowing for losses attending the conversion of energy in the dynamo, an approximate practical equivalent of 630 units of electrical energy may be allowed.

The energy expended in the electrolysers in the production of a unit quantity of 'active chlorine' varies directly as the resistance of the solution, and also increases as the concentration of 'active chlorine' increases.

Under average conditions, for the production of 1000 grams of active chlorine, we require a quantity of electricity equal to 1000 ampère-hours, which at a pressure of 3·5 volts represents 3500 units of electrical energy (watt-hours), equal to 5–6 horse-power-hours ; that is, the equivalent of 1 kilogram of ordinary bleaching powder is produced with an energy-consumption represented by about 2 horse-power-hours.*

Such figures appear to establish an economical advantage of 'electrolytic chlorine' prepared by any of the systems above described over 'bleaching powder chlorine,' prepared either chemically or as a by-product of the electrolytic manufacture of caustic soda.

But it must be borne in mind that the cost of the salt is a serious item, since only a fraction of the quantity actually used can be converted into 'active chlorine.' Moreover, the cost of power in this country, and the special costs of an electrolytic plant and its upkeep, prevent serious competition with bleach-

* Journ. Soc. Chem. Ind., 1892, p. 963.

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ing powder. On the other hand, in countries which have an abundant supply of water power, readily convertible, and which have no highly developed alkali industry, and therefore depend upon imported bleaching powder, the balance of advantage is in favour of electrolytic bleaching systems.

Permanganate Bleaching.—Although potassium permanganate has not yet found any application as a bleaching agent in paper making, it may be mentioned briefly here, because any considerable reduction in price would bring it into practical competition with the hypochlorites, especially since it has no 'chlorinating' action on lignified fibres. Potassium permanganate gives a violet solution, possessed of powerful oxidising properties, which breaks up in presence of strong acids and oxidisable matter according to the equation

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
('active' oxygen)

Such a reaction is, however, too severe for bleaching purposes, and the permanganate is therefore employed in neutral solution, under which conditions the quantity of 'available' oxygen is less, and brown manganese dioxide is precipitated in the fibres; thus

$$2KMnO_4 = K_2O + 2MnO_2 + 3O$$

The deposit of manganese dioxide has to be extracted from the bleached fibre by the action of an oxidisable acid, such as sulphurous acid or acidified sulphite of soda, the cost of which must be added to that of the permanganate. This 'clearing' action is expressed by the equation

$$2MnO_2 + 2H_2SO_3 = 2MnSO_4 + 2H_2O$$

The action of permanganate as a paper-maker's bleach has been carefully studied by C. Beadle,* who states that this agent possesses some very valuable characteristics. He found that the bleaching action of permanganate takes place almost instanta-

* 'Chapters on Paper-Making,' 2, p. 119.

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neously, whereas that of the hypochlorites is very sluggish. He found, moreover, that the bleaching efficiency of the 'active' oxygen of the permanganate is 5½ times greater than that of the 'active' oxygen of bleaching powder, and therefore that 1 lb. of permanganate will do the bleaching work of 10 lbs. of bleaching powder, whereas, according to the chemical equivalents, 4 lb. of permanganate should be equal to 7 lb. of bleaching powder.

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CHAPTER VII.

BEATING.

THE bleached pulp is still in the condition of 'half-stuff,' requiring a further and final treatment. If it were attempted to make paper from the pulp in the state in which it leaves the 'potchers' or 'steeping' chests, it would be found to be wanting in evenness of texture and other qualities which mark a well-made sheet of paper. This result is only secured by a process of disintegration and comminution, the main and immediate purpose of which is the complete separation of the individual fibres, which in the half-stuff still adhere to one another and are more or less agglomerated into masses. The fibres, thus separated one from another—a necessary condition for realising their felting and interlacing qualities in the formation of the paper—flow independently in the liquid medium.

Secondly, the ultimate fibres should be reduced to the optimum length, which length varies according to the class and substance of paper to be made.

These two effects, namely, the separation and reduction of the fibres, are produced simultaneously. At the same time, other physical changes are determined by the action of the knives of the beater-roll, resulting in the bruising and flattening of the ultimate fibres, and, in many cases, their further reduction, as by splitting longitudinally into smaller units, or fibrillæ. Where the beating is carried to extreme limits, as is frequently the case for high-class rag papers, such as bank note and cigarette papers, many of the individual or ultimate fibres are beaten out of all recognition.

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The manner in which the fibres become separated and mechanically reduced is determined not only by the methods of beating employed, but equally by the structural characteristics of the fibre acted upon. In this matter, each class of fibre has certain characteristics which can, in some measure, be foreshadowed by a careful study of Chapters IV. and XII.

The extent to which the ultimate fibre may have to be subdivided will depend, of course, upon its initial length. Thus, straw-pulp fibres are already so small, both in length and diameter, that they mostly escape disintegration. The esparto fibre, being somewhat longer, is occasionally cut asunder. On account of the smooth and flattened nature of the wood fibre, it is less frequently cut or bruised than might be expected. Very strong linen banks, and similar papers, contain fibres with an average length of 3–5 mm. After the most strenuous care has been exercised to draw out the fibres without cutting them asunder, they are found to be cut, on an average, into about six pieces. It is impossible, in the case of linen, hemp, and cotton, by any ordinary beating process, to separate the fibres without disintegrating them.

For strong papers it is necessary to avoid a cutting action as far as possible, the disintegrating or rending asunder being brought about by bruising and breaking, giving to the ends of the fibres a broken, splayed, or tangled appearance, which adds to their felting or strength-giving qualities.

Cotton is split by the bruising action of the roll at the point of rupture, into fibrillæ, showing an interlacing network or trellised appearance, but linen, on the other hand, is split into a bundle of longitudinal fibrillæ forming often a paint-brush-like end. Such deformation of fibres largely increases their strength-giving and felting qualities; on the other hand, if the beating is conducted so as to give a clean cut at the edge, the fibres produce papers of inferior strength, due to their inability when interlaced to grasp one another.

A fresh change takes place in the fibres as the result of their contact with the watery medium; the continual beating and agitation causes the cell-wall of the fibre to absorb water,

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and pass into the condition of a gelatinous hydrate. In proportion as this change is effected, the stuff is said to work 'greasy' or wet, an effect which may be regarded as due to a solution of water by and in the cellulose (hydrate).

Some celluloses are more susceptible of these changes than others; thus, linen pulp always has a greasy feel, and for this reason can be distinguished in the hand by the beater-man from cotton, which has not the same tendency.

For the production of strong papers, prolonged beating may be essential, not only in order that the fibres may be drawn out, but to produce this gelatinous effect, which is a matter of time. If half-stuff is beaten for a period of, say, from 40 to 150 hours, its condition approximates to that homogeneous, gelatinous mass which is obtained by the spontaneous setting of solutions of the sulpho-carbonates. This product, by draining, pressing, drying, and moulding, is used as structural material, and known as cellulith. This may be regarded as the extreme product resulting from prolonged beating.

Obviously, material beaten to work 'wet,' carries more water on the paper machine than 'free' stuff; it undergoes more shrinkage on drying, and gives to the finished paper increased rattle and hardness. This produces a less porous paper, the sheet being 'closed' in such a way as to reduce the amount of sizing required to give ink-resistant quality.

The instrument used for reduction of fibre material to finished pulp, as used up to the middle of the 18th century, resembled in action an ordinary pestle and mortar. Among primitive peoples a hand pestle and mortar, or its equivalent, in wood or stone, has been used from the early introduction of paper-making up to the present time. When water-power supplanted hand-power, the beating was accomplished by batteries of stampers, not unlike those used for quartz crushing. The mortar, which served for several stampers, was hewn out of the stem of a tree, made hollow by gouging. The stampers were lifted by cams on a shaft, and allowed to fall in succession. A mass of rags was placed in these mortars and operated upon for from 10 to 24 hours, water being allowed to trickle into the

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mill. Such disintegrating is said to have been superior to our modern system of beating, but the output was very small. Since the introduction of the Hollander about 1750, first in the Netherlands, then in Germany, and subsequently in this country, it has held its own up to the present time. The general principles on which it is constructed are the same to-day as in the early types, and as these general principles, for the most part, apply also to all other forms of beaters, a general description of the Hollander and its mode of action is fundamental. In passing, it would be as well to mention that the disintegration of raw materials, before the introduction of chemicals, was largely promoted by the fermentation processes to which they were subjected, resulting in the partial 'retting' or rotting of the fibre, which left less work for the beating engine to accomplish than at present.

The Hollander consists of an oblong trough, with semi-circular ends, with a partition or mid-feather running down the centre so as to form a continuous channel round which the stuff can circulate. Towards one end is situated the beating roll, on a horizontal axis. The roll is provided with a number of knives or bars. In general construction and design it resembles a 'breaking' engine, already described and illustrated (p. 121). The bottom is shaped as shown in Fig. 21, so as to enable the stuff to circulate when the roll is set in motion. The Hollander varies in size according to requirements, its size is generally stated in terms of the pounds of dry fibrous material it is capable of holding in the form of pulp. The smaller beater as used for hand-made mills will carry from 1 to 2 cwt. In an ordinary rag machine mill, the beaters carry from 3 to 4 cwt.; in new mills working wood-pulp, the beaters sometimes hold 10 or 12 cwt. The largest Hollanders carry from 20 to 30 cwt. of dry stuff, according to the nature of furnish. The bed-plate is situated at such a height that when the beating-roll is in contact with it the shaft is just clear of the flow of the stuff. The diameter of the beating-roll will vary anywhere from 3 ft. to 4 ft. 6 in. and the width of the roll from 2 ft. 6 in. to 4 ft. 6 in. and upwards. The width of the roll is only slightly less than

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that distance from the side to the mid-feather, leaving only about half-an-inch daylight between.

In order to prevent lodgment of stuff, head-strips of metal, called 'bangers' are screwed on the side of the rolls, which, in their revolution, drive any stuff forward.

The beater is rounded or dished at the bottom. All sharp corners are avoided in order to prevent lodgment of stuff. An ordinary beater is about 2 ft. deep at the shallow end, with another 5 in. at the back-fall end, at which point the stuff is at its highest level, falling, as it travels, back to the roll.

The circulation of the stuff is primarily promoted by the projecting bars of the roll, which, for this purpose, are arranged in groups, which, in their revolution, act like paddle-propellers

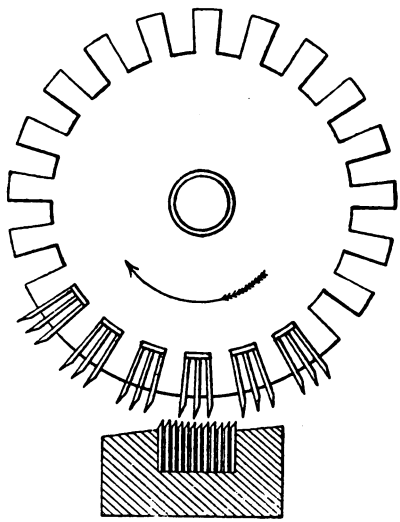

FIG. 33.

(Fig. 33). These lift the stuff over the back-fall, from whence it travels, by gravitation, completely round the beater to the other side of the roll.

The early Hollanders were driven by cog-wheels, the raising and lowering of the roll being worked by a gear under one

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bearing, the other bearing, next the cog-wheel, being, of necessity, a fixture. This resulted in irregular wear on the bed-plate. Of recent years both bearings are provided with gearing, whereby they are raised and lowered simultaneously, the rolls being driven by belts from pulleys fixed to shafting underneath the floor. Close to the bed-plate is a perforated plate over a hollow channel running across the bottom. As the stuff passes over this plate, any heavy particles, such as broken buttons, metal particles and heavy dirt, pass through and are periodically removed by opening a cock underneath.

The early beater rolls were made of wood; the roll being light, especially when immersed in water, it exerted a limited pressure on the bed-plate. It was impossible, therefore, for the beater-man to spoil the stuff by over-pressure on its bed-plate. He could, without injury, lower the roll down completely on the bed-plate in the early stages of the beating. Now, the rolls are made of metal and weigh many tons, it is necessary to let the roll down gently at different stages of the beating; the wooden rolls made beating a slow process, with metal rolls the beating can be accomplished only too quickly.

The trough, which was formerly made of wood, is now more often made of cast-iron, but sometimes of cement. For best papers, the metal beaters are lined with lead. The covers to the beater-rolls are generally made of wood, but sometimes of zinc or other metals.

The beater-roll is two-fold in its action. Its chief function is to draw out, disintegrate and crush the material as it passes between the fly-bars and the bars of the bed-plate. Its second function is to effect the circulation of the pulp, which it does by acting as a paddle-wheel or bucket-lifter. On examining in section (p. 121), it will be seen that the stuff carried by the fly-bars would be lifted over the back-fall, but on account of the rapid rotation of the roll, some stuff makes a complete revolution, and falls again in front of the roll, impeding the circulation, as can be seen if the splash-board is lifted.

This defect is to a large extent obviated by certain additions and modifications of structure embodied in 'Tait's Patent Beat-

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ing Hollander.'* The essential modification consists in heightening the back-fall, with the introduction of a guard, concentric with the roll, thus forming a narrow passage for the passage of the stuff, ensuring its continued circulation and preventing its falling back on the roll. By avoiding this local churning action, the entire contents of the beater pass more frequently through and under the roll. The structural improvements in question are indicated in the shaded portions of the accompanying sectional sketch elevation (Fig. 34).

A is the trough, B the partition therein, C is the shaft and D the beater roll, E is the shield with a curve guide F, from which is hung by hinges a flap G. H is the uprising incline of the bottom to the dead-plate I, the bottom then being curved at J to the neck K, from which is the descent-plate or back-fall

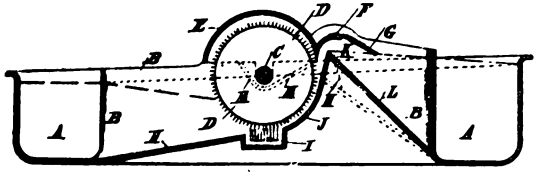

FIG. 34.

L. This may be at any angle such as is indicated by full lines, the dotted lines showing the height at which the back-fall of an existing beater engine is carried; the additional height can be made to form the narrow passage by building up on the existing one by a lump such as that shown by the curved dotted line N. M is the guard in the open return part of the trough A and under the shaft C.

The space between the top edge of the back-fall L and of shield E and guide F is of such shape and narrow, but of the full width of the roll E, to prevent the 'stuff' falling back between the roll E, curved plate J, or of being carried round by the roll E, whereby the stuff has a better travel and circula-

* English patent 23,130, 1892. Thomas Tait and John Hood.

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tion than usual, and passes oftener and more regularly between the roll and the plate.

The rapid churning, occasioned by the roll, although it consumes a considerable amount of power, performs at the same time a useful function. It beats or forces air into the stuff, and also maintains a condition of continual friction

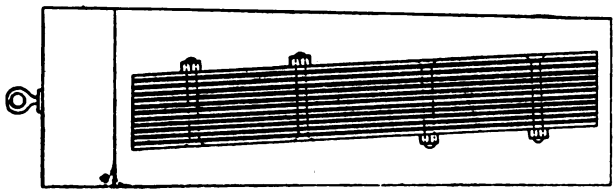

FIG. 35.

throughout the mass of fibres and water which aids the hydration already referred to, i.e. the production of 'wet' stuff, which the beating alone could not accomplish in the same period of time.

The bars in the bed-plate vary from two to twenty. They are placed at an angle (Fig. 35), whereas those of the beater roll (Fig. 33, p. 180) are placed parallel with the axis of the roll. Fig. 36 shows the manner in which the knives of the bed-plate are fixed. The greater the angle of inclination of the two sets

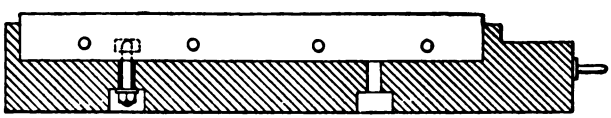

FIG. 36.

of knives, the more rapid is the reduction of the stuff. Conversely, a slower reduction of the fibres, by bruising and tearing rather than by actual cutting, is favoured by decreasing the angle of inclination; such an arrangement, of course, absorbs a greater amount of power. Absolute parallelism is to be avoided, on account of the danger of interlocking and of breaking the bars under the shock of contact. In order to increase the

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angle, knee-plates or elbow-plates are often used (Fig. 37), and sometimes zigzag plates. The greatest cutting efficiency is got when the two sets of bars meet each other at an angle of 45°. Sharp angle-plates are particularly serviceable when the fibres require to be beaten rapidly, as for blotting and other soft papers. Where the point of the angle touches the fly-bars the latter wear away more rapidly, forming indentations in the bars and necessitating their more frequent sharpening. Steel bars are sharpened by chipping with a cold chisel. Bronze bars can be planed *in situ* by attaching a small milling machine.*

The angle plates have an additional effect. They promote a more thorough mixing of the stuff. Thus, if the apex of the angle of the plate points in the direction in which the roll is

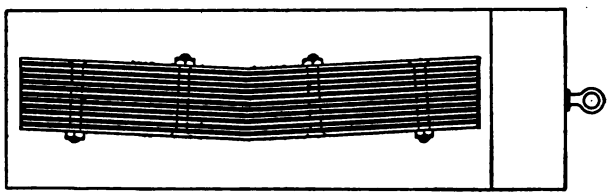

Fig. 37.

rotating it tends to cause the stuff to travel from the mid-feather and outside of beater to the centre of the stream. *Vice versâ*, if the angle were placed in the opposite direction, the tendency would be to make the stuff flow from the centre to the outside.

The rate of travel of the stuff depends largely upon its consistency, and as this varies at different stages of the beating, the travel and circulation also vary.

The beating power of the Hollander is dependent, not only

* We are indebted to a prominent paper-maker for the information that bronze bars wear down much more slowly than the harder steel bars: for instance, a set of bronze bars lost $\frac{5}{8}$ inch in 8 years, whereas steel ones lost $\frac{3}{4}$ inch in 1 year. Moreover, whereas steel bars wear round on the cutting edge the bronze always maintains a square edge, and the lowering of the roll must be performed with great caution for fear of cutting the fibres.

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upon the number of fly-bars in the beater-roll, but also upon those in the bed-plate. It can be expressed as the product of the length of the roll-bar, the number of bars, the number of bars in the bed-plate, and the number of revolutions which the roll makes per minute. This expression represents the number of foot-strokes per minute, a convenient expression as a basis of comparison of different beaters.

The rate at which the fly-bars of the beater-roll pass those of the bed-plate is commonly described as the circumferential speed. It is generally recognised that this should be a fairly constant quantity, and approximating to 2000 ft. per minute. Consequently, the larger the diameter of the roll, the slower the revolution of the shaft. This is a factor which has to be studied in order to promote a sufficient circulation consistent with high beating capacity. This, however, does not hold good for other forms of beaters, notably, those with independent means of circulation, later to be referred to.

The 'breaking in,' resorted to in the case of rags and similar stock, is done in a separate engine, called the breaker (page 121). This, although similar in construction to the beater, is provided only with blunt knives on roll and bed-plate. The breaker is provided with a drum-washer. This is a revolving drum, covered with wire gauze over a backing. The wash-water, which passes in just in front of the roll, is removed through the drum on the opposite side of the beater. The suction through the drum was at one time promoted by a siphon, but now by means of internal buckets, as shown in Fig. 21. An effective way of removing water, now abandoned on account of the loss of fibre occasioned, was to place a wire screen in the cover of the beater-roll, which is above the back fall; against this screen the stuff was projected by the force of the roll. In coming in contact with the screen much of the dirt was loosened and passed through the meshes.

In the beating operation proper, when first the engine is furnished, the roll is, to use the current expression, 'put down light' for half an hour or so. The beater-man then gradually lowers the roll on the bed-plate until, towards the end of the

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beating, the roll is 'hard down,' which means that it is exerting the pressure of its full weight. Ten minutes before emptying, the roll is lifted somewhat to clear or 'refine' the stuff.

A large proportion of the power necessary for driving a paper mill is absorbed in the beater-house, consequently any economies that can be effected in this department deserve particular study. Such economies can only be effected when the nature of the power consumption is properly understood. Useful information can be gleaned from diagrams of the power absorbed. (Fig. 38.)

Diagram A shows variations in power with the Hollander, when the roll is allowed to brush lightly. Diagram B, the same when the roll is put down at different periods during the beating. Diagram C shows a diagram with the Taylor beater when lightly applied, and Diagram D, when the roll is more heavily applied for a short period. To the power so consumed must be added in each case that required to run the respective beaters empty. The diagrams (Fig. 38), which were used in researches on the 'Theory and Practice of Beating,' are recorded by means of a dynamometer invented by Mr. A. Masson, and are reproduced here by kind permission of Messrs. Masson, Scott and Co., Ltd.

With the Hollander these show that the power consumption is chiefly dependent upon the position of the roll, or the amount of pressure exerted by the roll upon the bed-plate. For any fixed position, as is evident from the diagrams, the power consumption remains fairly constant, although the stuff is altering in its consistency. Immediately the roll is further lowered the power consumption increases, and remains again constant until the roll is again lowered, and so on. The disadvantage of the Hollander, from the point of view of power consumption, is due to the fact that it is necessary, as the beating proceeds, to increase periodically the pressure on the roll, and, consequently, the power required to drive it.

With certain forms of beaters it is possible to adjust the roll at a constant elevation with just the right pressure of roll on bed-plate to give a satisfactory as well as an economical

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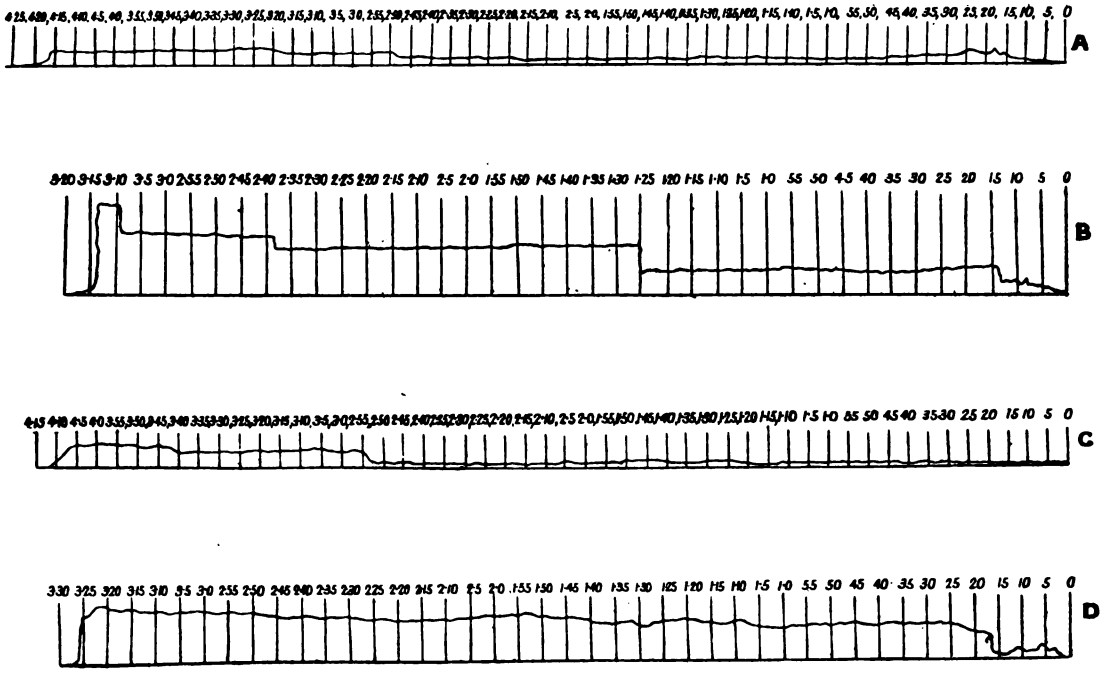

FIG. 38.

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result. Such a mode of beating can be applied to the short fibred half-stuffs, such as straw, esparto, and some forms of wood pulp.

The introduction of the electric drive has rendered it possible to take records of the power consumption of individual beaters, which by the older methods of taking indicator diagrams was not possible. Now that the beater-man can see at a glance, at any moment, what his machines are individually absorbing, satisfactory progress is being made in the direction of more stringent economies; nevertheless, much remains to be done in this direction.

Recent trials tend to show that for any given class of material in the Hollander the power consumption per ton of stuff diminishes as the size of the engine increases.

With rag pulps there is, however, a limit to the size of the beater, on account of large rolls being found to produce beaten stuff unsuitable for fine papers.

The amount of power expended in the Hollander with different kinds of material has been recorded in a few instances.

The following table shows the total expenditure of power in breaking, beating and refining, and the ratio of power consumed in each class of material, lowest as 100.

—	H.P.H. per cwt. of Stuff Beaten.	Relative Power Consumption when lowest equals 100.
Sulphite wood	12·52	100
Manila rope	23·36	187
New jute threads	26·34	210
New twine ends	46·71	373
New linen threads	53·83	431
New rags	63·61	509

In interpreting these figures it must be borne in mind that the power consumed depends not only on the kind of material, but also on the nature of the paper to be made from it, i.e. on the manner and duration of the beating, variations in respect of time being very great.

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As regards the distribution of the power absorbed, the following is instructive :—

	H.P.H.
The friction of steam engine and shafting . .	4·660
For friction of empty beater	2·727
For circulation and agitation of stuff . . .	14·560
For beating proper, and friction of bars against bed-plate	15·843
	37·790

The subject of the circulation in the Hollander is too complex to discuss here in detail, but the following table, based on careful trials, shows relative changes in the rate of circulation during the beating, and when the initial speed of outside flow is taken as 100.

—	Beginning.	Half-time.	At finish.
Outside	100	110	120
Middle	123	140	151
Inside (mid-feather) . . .	103	117	127
Mean	109	122	133

Mean of all = 121.

In the following table we give, in two instances, the amount of power absorbed, as distributed between the three processes of breaking, beating, and refining.

Material.	Breaking h.-p.h. per cwt.	Beating, h.-p.h. per cwt.	Refining. h.-p.h. per cwt.	Total of Breaking, Beating and Refining h.-p.h. per cwt.	Breaking.	Beating.	Refining.
					p.ct.	p.ct.	p.ct.
New Twine Ends	23·40	19·45	3·86	46·71	50·1	41·7	8·2
New Rags	44·18	15·30	4·13	63·61	69·3	24·1	6·6

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In some respects the Hollander is wasteful. This has been abundantly proved from comparative trials made between the Hollander and Taylor beaters, and others, as well as by careful analysis of the total power consumption in comparison with that which is usefully expended. In one instance it was conclusively proved that at least 26 p.ct. of the power was entirely wasted in the Hollander. To arrive at such deductions much careful experimental analysis is needed. For fuller information on such questions we would refer our readers to articles on the 'Theory and Practice of Beating.'

In the table opposite, taken from the catalogue of Messrs. Joachim and Son, of Schweinfurt, Germany, are set forth the relations between the dimensions and capacities of Hollander beating-engines of modern design. These data will be found useful in calculating the cubical contents of other beaters of intermediate dimensions. The diameters and weights of the rolls, the speeds of revolution, and the number of knives in the rolls and bed-plates may be taken as representing the most efficient combinations of conditions for the circulation and beating of the stuff.

For certain kinds of stock it is admissible to use large Hollanders carrying up to 20 cwt. of wood pulp, which can be thickened up to 30 cwt. with papers. Recent trials show that such engines are more economical than those of smaller dimensions.

In Umpherston's patent engine great economy of space is effected by causing the pulp to travel over and under the backfall (*a*, Fig. 40). Another advantage is that the stuff circulates freely with less water than in the ordinary forms, thus increasing its output. It is also claimed that the pulp is beaten with less power, and, as it is less liable to lodge in corners, it is more evenly beaten.

The construction of the engine will be readily understood by reference to Fig. 40. The direction which the stuff takes is indicated by the arrows.

When it was discovered that an independent means of circulation could be made use of, it was no longer necessary to

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Charge of Air-dry Pulp.		Cubical Capacity.	Trough.			Roll.			Bed-plate.		Driving Pulleys.		Revolutions per Minute.
4 p.ct. Concentration.	5 p.ct. Concentration.		Length.	Width.	Depth.	Diameter.	Width.	No. of Knives.	No. of Knives.	Breadth of Knives.	Diameter.	Width.	
Kilos.	Kilos.	Litres.	Metres.	Metres.	Metres.	Metres.	Metres.			mm.	Metres.	Metres.	
52	65	1300	3·000	1·300	0·550	0·800	0·600	54	10	5	0·900	0·175	200
72	90	1800	3·400	1·500	0·575	0·900	0·700	63	15	5	1·000	0·175	180
100	125	2500	3·800	1·600	0·650	1·000	0·750	69	15	5	1·100	0·200	160
135	170	3400	4·200	1·850	0·700	1·125	0·850	78	18	7	1·250	0·200	150
160	200	4000	4·500	2·000	0·775	1·200	0·925	84	18	7	1·300	0·250	135
230	290	5750	5·000	2·200	0·850	1·350	1·025	90	20	7	1·500	0·250	120
320	400	8000	5·500	2·400	0·925	1·500	1·125	96	22	8	1·650	0·300	105
400	500	10000	6·000	2·600	1·050	1·600	1·225	101	24	8	1·800	0·350	100

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construct the roll so as to propel the stuff. In the Taylor, Reed, Acme and other beaters this is effected by an independent agency such as a fan or helical propeller, by means of which it is circulated round the beater. It is merely necessary to maintain sufficient difference of levels to cause the stuff to overflow the bed-plate at the rate at which the roll is able to conduct the beating; the circulator maintains this difference of levels. The bars of such beaters are placed close together and at regular intervals. The bars of the rolls do not require to be arranged in groups, nor to project beyond a short distance, as they are not concerned in the circulation of the stuff. They furthermore do not require to be bevelled on the edge, being rectangular in section. The more exact distance of bar from bed-plate needs to be studied, but with short fibres the beating can be conducted throughout without alteration of adjustment. Such practice results in the production of stuff in quantities not attainable in the Hollander. The economy of such beaters over the Hollander is most marked in such materials as straw, esparto and soft wood pulps and mechanical. With rag papers the Hollander still holds its own. The reason for this lies in the fact that the efficiency of a beater should not be judged on a quantitative basis only. In fact, for certain purposes, the 'patent' beaters and even Hollanders of large capacity may be *too efficient*. For much of the power which is apparently 'wasted' in a small Hollander, the paper-maker obtains a return in the form of 'quality,' i.e. length of fibre, production of fibrillæ, and hydration of the cellulose.

The Acme Beater (Bertram and Shand's patent) embodies original features in construction and working, of which the more essential are (1) the elevation of the beating-roll from the main pulp channel; (2) the provision of a screw propeller for elevating the pulp from the main channel to the roll; and (3) the division of the trough into two channels, the upper of which contains the roll, by a partition which can be made to swing in a practically perpendicular position. This arrangement simplifies the emptying and washing out of the engine. These more important particulars are set out in the annexed

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figure (Fig. 39), which represents a longitudinal section of the beater. We are indebted to the firm of Bertrams, Limited, of Edinburgh, the makers of this beater, for the drawing, and for information respecting this and other machines; and we take this opportunity of advising our readers of the important 'Illustrated Catalogue of Paper Mill Machinery,' published by this firm, which will be found to contain a complete descriptive account of the paper machine and all auxiliary appliances, in their most improved and modernised forms.

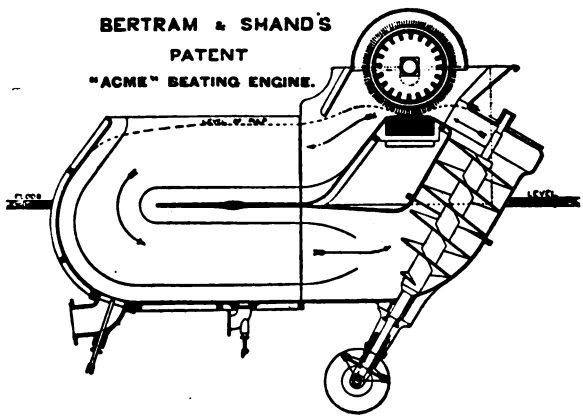

FIG. 39.

The use of stone beater-rolls is not new; stone bed-plates have been used for many years in conjunction with metal bars. The introduction of the basalt lava stone, however, marks a new departure. The use of a complete roll of this stone is now abandoned in favour of removable bars. Provided that the wear and tear on the stone is not excessive it shows notable advantages over metal bars, the most marked being the getting off of the material in about one-half of the time. So far, however, this has not been accomplished without greater power consumption, and the cost of power per ton of beaten stock

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about the same as when metal bars are used. The explanation of the greater beating capacity of the stone is perhaps to be found in the fact that the innumerable pores in the stone present continuous beating surfaces independent of the width of the bar. In its action it may be regarded as a kind of combination of Kollergang and beater-roll. No doubt the stone roll requires different manipulation from ordinary rolls to avoid fracture or disintegration; under favourable circumstances it

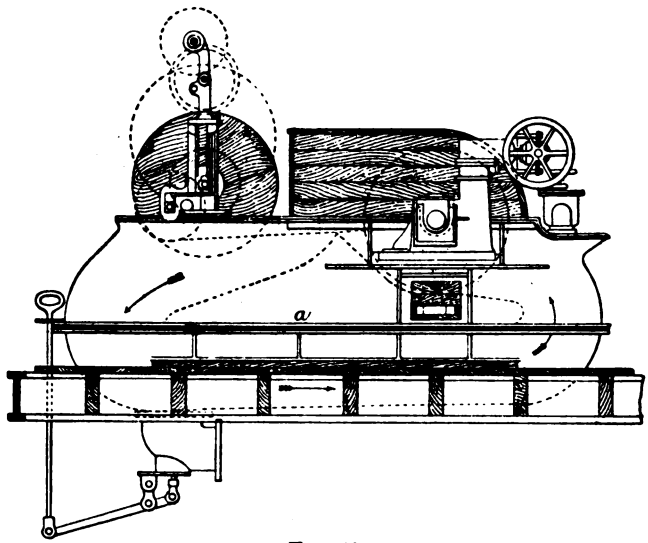

FIG. 40.

has shown only slight and uniform reduction in diameter in constant work.

The Umpherston Beater, Fig. 40, is really a modification of the Hollander, whereby the stuff is made to return underneath, the beater-roll promoting the circulation.

The Masson Tower Beater, in which the stuff circulates in a vertical upward and downward direction, altogether avoids lodgment, and reduces skin friction to a minimum, and by reason of the circulation of the stuff from the centre to the

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circumference at the top to the centre at the bottom, a complete admixture is assured. (See page 132, Bleaching Towers.)

The reason of the larger output from beaters with independent circulator can be readily grasped by the student if he calculates foot-strokes per minute, and compares them with those of Hollanders, details of which can be found in 'The Theory and Practice of Beating.'

The beater-man does not concern himself with theoretical considerations. The appearance and feel of the stuff in the beater he considers to be a sufficient guide to him during the early stages. The Hollander has the advantage of being open to his view, so that he can see the stuff, watch its circulation, and judge of its progress. If the circulation is retarded he takes a wooden paddle which he sweeps along the bottom, round the outside, and against the mid-feather from both ends, this being done occasionally until sufficient circulation is assured. The paddle removes any obstructions in the way of lodgments. Sometimes the lodgments are pushed forward by a longer wooden contrivance with a flat end, which is also made use of for completely emptying the beater and swilling it round with water.

The beater-man judges the pressure of roll on bed-plate by the feel or sound, either by putting his foot on the bed-plate or his hand on the wheel, or, better still, by the use of a wooden stick, one end of which is placed rigidly against the metal hook on bed-plate and the other to his ear. As the beating nears completion the length of the stuff is roughly judged by drawing a wire through it and noting how it hangs to the wire, or more roughly by pushing a paddle edgewise through the stuff and noting how it clings. Near the end of the beating the beater-man takes a hand-bowl in each hand, one he dips into the stuff so as to secure a small, but average sample, the other he fills with clean water which is poured into that containing the stuff, and periodically, whilst pouring it to and fro, increased in dilution by the addition of more water until so thin as to render the individual fibres separately visible. Whilst this is poured slowly over the lip of the hand-bowl he examines

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minutely the fibres, to see whether they are of the required length and qualities. At this stage there will be occasional knots and clusters, these he gets rid of by raising the roll so as just to brush the surface of the bed-plate, and again examines the stuff in the manner above described before emptying into the 'stuff-chest.'

The state of preparation of the stuff is controlled not only by the manipulation of the beater-roll, but also by the dilution of the pulp. The actual limits of variation in this respect are not very great—the proportion of water ranging from 18 to 33 times the weight of the fibre—but the influence on the result is very marked. With very dilute pulps, every stroke of the knives results in the actual division of the fibres between them, and the reduction of the stuff takes place in a minimum of time, and with a relatively low consumption of power. Such conditions produce a 'free-beaten' pulp. With very stiff pulps, on the other hand, the mass of fibres between the knives may resist the shearing pressure of the stroke, and the majority of them will escape actual division, being merely crushed, flattened, and split. Under these conditions the preparation of the stuff requires a very much longer time, with correspondingly increased consumption of power, and the pulp then becomes 'wet-beaten' or hydrated.

If a *long free* stuff is required the bars must be fairly sharp, and the roll brought to its proper and final position fairly quickly, but never hard down. Such stuff can only be got from certain materials, such as new cottons.

If a *long wet* stuff is required, dull tackle is used and the beating prolonged to, say, double the ordinary time; strong linens and bleached half-stuff from flax produce this effect with above treatment. If the stock is left about the mill, particularly in a basic and wet condition, the effect is accentuated.

If a *short wet* pulp is required the above-mentioned treatment is partially carried out until the wet effect is thoroughly produced, then the roll is lowered to reduce the fibre to the requisite length.

A *short free* pulp is produced by having sharp tackle, that

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is, the bars of the roll and bed-plate must be sharp; the cutting effect is much accelerated by the use of angle and zigzag plates above referred to. Tender stuff, such as muslins, and any stuff of a brittle or tender nature, lends itself particularly to this treatment. The stuff must not be about too long in contact with alkalis, or in the various preliminary stages. The beating must be conducted by putting the roll down hard so as to get the stuff off in as short a time as possible, and the beaten stuff should be passed over the machine without much delay. Rising temperature in the beater tends to promote 'free' working; conversely, wet working is conserved by keeping the temperature down, and, of course, is increased by the beaten stuff lying in the chest, as when left over Sunday.

As mentioned above, the limits between which the concentration of the stuff can be varied, with the object of controlling its character, are not very wide. A certain concentration, depending on the nature of the material, is necessary to insure an efficient circulation in the Hollander; on the other hand, above a certain concentration the stuff is too stiff to circulate. With an independent means of circulation, however, the concentration of the pulp can be increased beyond the limit indicated above. When it is important that the stiffness of the pulp should be maintained throughout the whole period of beating, further additions of half-stuff or broken papers may be made as the stuff thins down.

Certain chemical substances influence the beating; alkaline compounds, such as soda, and silicate of soda, promote 'wetness.' On the other hand, substances of an acid nature, such as alum, promote free working of the stuff. The use of various chemical substances as auxiliary to beating has not received much attention. Results, so far, appear to indicate that much might be done in this direction, both in producing special effects and in economising power or increasing output.

The factor of pressure of roll on bed-plate is one of considerable importance. This can be calculated when the weight of the roll is known and the superficial area of the bars of roll and bed-plate, for the limiting position of the roll. Thus,

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with a given number of foot-cuts per minute must be taken into consideration the pressure in pounds per square inch that the roll exerts upon the bed-plate, in order that the beating capacity may be arrived at; but it cannot be said that the beating capacity is in direct proportion to the pressure of the roll, and, seeing that the result to be achieved varies enormously with particular requirements, limiting the pressure that may be exerted, the mathematical treatment of the beater is liable to the danger of leading to unwarrantable conclusions.

The word 'beating' is, perhaps, hardly descriptive of the various processes or treatments involved in the reduction of fibrous materials, and, perhaps, no comprehensive term can be found for these several processes. These vary from actual cutting of the fibres in the manner of a pair of scissors to that of bruising and crushing, and between these two extremes we have the mere drawing out or separation of ultimate fibres, the flattening as by rolling, and splitting into fibrillæ. All these different processes are involved in every case of beating, although the conditions of beating, as well as the nature of the material, assist to determine which is to predominate. The mechanics of beating is, therefore, complex, and incapable of scientific treatment, in so far that it does not lend itself to any form of numerical expression.

'Refining' and Refiners.—The operation of refining, as originally conducted, and as generally practised at the present time, is used for clearing the stuff, i.e. performing just that operation which is ordinarily conducted in the beater when the roll is lifted and made to brush out the stuff just before emptying. In such cases only a small amount of the power is expended in the refining operation.

It has become the practice in some mills to put an increasing amount of work upon the refiner, and, consequently, less upon the beater.

The 'Jordan,' 'Horne' and 'Marshall' refining engines consist essentially of hollow cones provided internally with fixed bars, in which rotates a solid cone provided with bars; the stuff passing between these bars is brushed out. If a small

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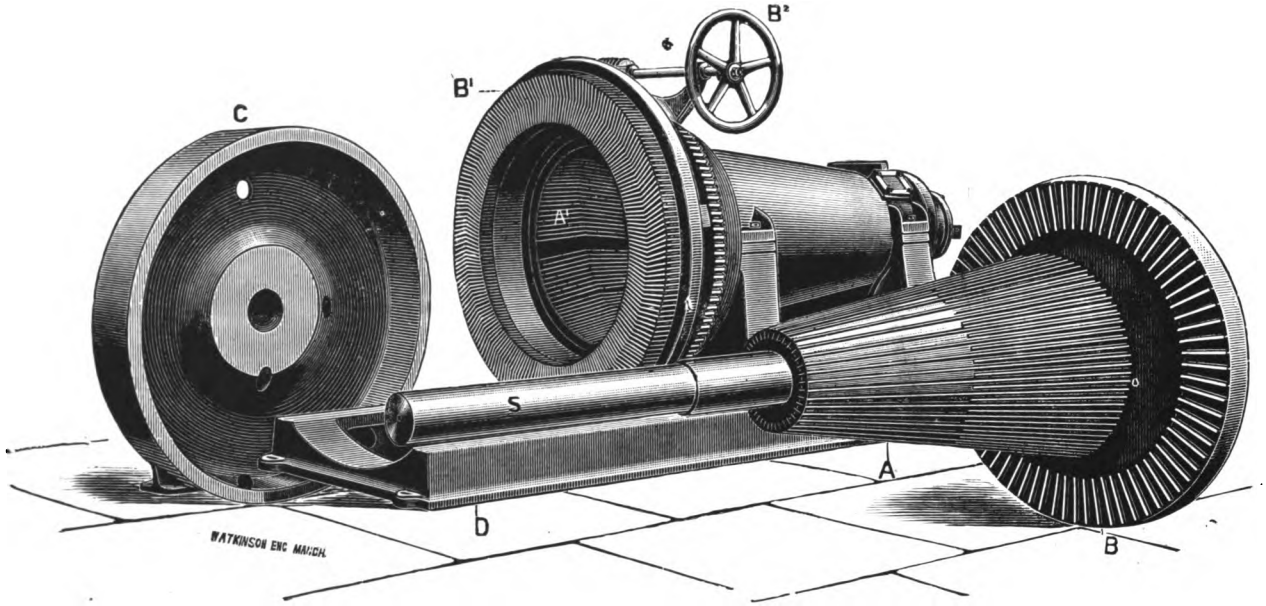

FIG. 41.

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amount of brushing or clearing only is required the stuff is passed rapidly through, the reduction being controlled largely by the flow, but also by the pressure of the revolving bars against the fixed bars. Like Hollanders, and other types of beaters, there is a certain rate of output and pressure on bars which will perform the necessary brushing out with a minimum expenditure of power. The specific action of these refiners depends to a large extent on the fact that the circumferential velocity increases from the inlet at the narrow end to the outlet at the wide end; thus the fibres pass through under a tension which draws them out straight and parallel.

The Marshall Refiner, as illustrated in Fig. 41, consists of the two essential parts: A, a cast-iron cone revolving within the fixed cone A^1, fitted with steel angled knives, and B, a cast-iron disc revolving at an adjusted distance from the stationary disc B^1, also fitted with angled knives held in position by hard wood wedges or fillets. The work of the former is to reduce the fibres to uniform length, the disc portion of the engine then reducing the stuff in the plane at right angles, that is, by breaking up fibre-aggregates, or even splitting the fibres themselves. Each of these parts having, moreover, a separate adjustment, the work of the engine may be thrown on the one or the other, according to the requirements of the stuff and of the quality of the paper to be made. It is claimed for this engine that it effects a considerable economy in the time of beating, in addition to the advantages resulting from a more uniform preparation of the stuff. It must be remembered, however, that in paper-making, as in the processes incidental to the preparation of textile materials, there are effects which time only can produce, and that, therefore, the refining engine is at the best only capable of substituting the work of the ordinary beating-roll within limits.

Fig. 42 illustrates Pearson and Bertram's Refiner, made by Messrs. Bertram, Ltd., in elevation and when parts are detached. It consists of a central disc, rotating between two stationary discs. One is securely fixed to the back part of the case, while the front one is fixed to a plate, and is adjustable by means of

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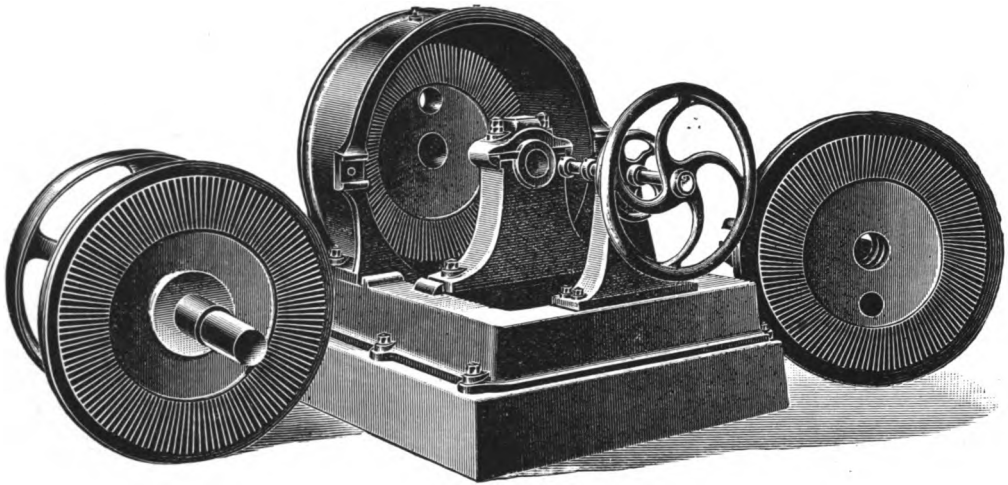

FIG. 42.

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the hand-wheel. The bars, made of bronze, are fitted into dovetailed grooves in the discs, and are each about 6 in. long.

The pulp is led through the inlet-pipe to the first stationary disc, after which it flows outwards between the two faces into the outer portion of the case, then between the front faces towards the outlet pipe in the second stationary disc, the pulp thus passing twice between the bars. Proper reduction and uniformity of stuff is secured owing to the fact that before leaving the refiner it is compelled to pass through the bars against the centrifugal force. This insures that lumps of fibre on entering the bars are immediately thrown outwards again, and prevented from passing through the machine until reduced to smaller particles, when they easily pass against the centrifugal force. For certain fibres this refiner can be arranged with adjustable gear, so that the inner faces can be made to cut the fibres and the outer faces to do the refining proper. In an ordinary sized refiner there are between 500 and 600 bars.

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CHAPTER VIII.

SIZING, LOADING, COLOURING, ETC.

We have now to describe various auxiliary preparations which are carried out in the beater, each contributing some important quality to the finished sheet of paper.

Excepting in mills where the pulp after bleaching is treated on the presse-pâte, the bleached half-stuff as furnished to the beater often contains an excess of bleaching compounds, which can be removed in two ways, viz. by washing or by decomposition with an 'antichlor.' The first method has the advantage of removing not only the bleach, but also the chloride of calcium, existing ready formed, and resulting from the decomposition of the calcium hypochlorite in the bleach. On the other hand, this method takes some time, and consumes a large amount of water, which in some mills is a matter of considerable importance. Where practised, the beaters are provided with one or more drum-washers (see Fig. 21). An additional objection to this method lies in the fact that a certain quantity of fibre passes through the meshes of the wire-cloth covering the washers, and is thus lost.

The more usual plan is to remove the residual bleach by decomposing it with an 'antichlor.' A substance frequently employed for this purpose is sodium thiosulphate, which, in presence of calcium hypochlorite, is oxidised to sodium sulphate, with formation of calcium chloride. Double decomposition then takes place between these salts, with formation of calcium sulphate and sodium chloride. The reactions which

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take place with oxidation to sulphate may be expressed by the following equation :—

$$2\,(Ca(ClO)_2) + Na_2S_2O_3 + H_2O = 2CaSO_4 + 2HCl + 2NaCl.$$

Calcium hypochlorite. Sodium thiosulphate. Water. Calcium sulphate. Hydrochloric acid. Sodium chloride.

The above decomposition does not accurately represent the action of bleach upon sodium thiosulphate. If the solutions employed are highly dilute, the decomposition may take place in another direction, viz. :—

$$Ca(ClO)_2 + 4Na_2S_2O_3 + H_2O = 2Na_2S_4O_6 + 2NaCl$$

Calcium hypochlorite. Sodium thiosulphate. Water. Sodium tetrathionate. Sodium chloride.

$$+ 2NaOH + CaO$$

Caustic soda. Lime.

At the particular degree of dilution which occurs in a beater, the bleach is held to be decomposed almost entirely according to the first of the equations ; from which, on calculating, it will be seen that 158 parts of sodium thiosulphate are equivalent to 286 parts of calcium hypochlorite. As commercial sodium thiosulphate contains 36·3 p.ct. of water, and bleaching powder 35 p.ct. of calcium hypochlorite, on the basis of 35 p.ct. available chlorine, it follows that 248 parts of the former are required on this equation to neutralise 817 parts of the latter.

Within the last few years other forms of 'antichlor' have been introduced, such, for example, as the various sulphites and bisulphites. Typical of these is sodium sulphite, which, in its ordinary crystallised form contains 50 p.ct. of the actual sulphite, as may be calculated from the formula of the salt $Na_2SO_3 7H_2O$. More concentrated forms are prepared by the action of sulphurous acid upon soda ash. It is obvious also that calcium and magnesium sulphites may be used to replace the more expensive sodium salt.

Sulphites are converted by the action of bleach into sulphates, thus :—

$$Ca(OCl)_2 + 2Na_2SO_3 = CaSO_4 + Na_2SO_4 + 2NaCl.$$

Calcium hypochlorite. Sodium sulphite. Calcium sulphate. Sodium sulphate. Sodium chloride.

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From this equation it will be seen that 252 parts of sodium sulphite will neutralise 143 parts of calcium hypochlorite, or 409 parts of bleaching powder. Assuming that crystallised sodium sulphite contains 50 p.ct. Na_2SO_3, the same amount of bleach would require 504 parts. Comparing these numbers with those given above for sodium hyposulphite, it will be seen that 409 parts of bleach require for neutralisation 124 parts of sodium thiosulphate and 504 parts of crystallised sodium sulphite, or proportionately less of stronger products.

So far as we are aware these reactions have not been systematically investigated as they actually occur in the beater. In such an investigation it would be necessary to take into account the concurrent oxidations due to atmospheric oxygen dissolved in the water and beaten into the pulp under the action of the roll.

Sodium sulphite is preferred to sodium thiosulphate by most paper-makers, notwithstanding the fact that even in its most concentrated form nearly three times as much is required to produce a certain result. It is found that when it is used the wire-cloth of the machine is preserved for a longer time than if sodium thiosulphate is employed. This may be due to the fact that with the latter a certain amount of free acid is always formed, which of course would act injuriously on the wire; whereas, when sodium sulphite is used, the products of decomposition are neutral salts without any action upon metals. (See the above equations.)

Hydrogen peroxide has been used to some extent as an 'antichlor' with satisfactory results. The only objection to its use is its relatively high cost.

Whichever variety of 'antichlor' is used, an excess should be carefully avoided, as all act more or less upon the size and colouring matter added to the pulp subsequently. The quantity is easily adjusted, either by an actual estimation of the 'chlorine' in the pulp and calculating therefrom, or the 'antichlor' may be added gradually, testing the stuff from time to time with the iodide test solution (p. 162).

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Sizing.—If the celluloses, reduced by the beating process to the condition of ultimate fibres, or further disintegrated by tearing and cutting to 'artificial' units of suitable length, are put together into a sheet or web, the product will be a 'blotting' or bibulous paper. Such papers have a well-known use; and 'blottings' are in effect made from cellulose pulps with the addition of a small proportion of starch, added to the beater in the form of starch paste, and for the purpose of adding a certain 'binding' quality to the fibres. Such papers, in addition to their absorbent properties for liquids, are 'soft,' relatively weak, and altogether unsuited to uses involving mechanical wear and tear.

Writing papers on the other hand have, as is well known, a totally different texture and 'handle,' and they have a certain water and ink-resisting quality: that is, they are required to oppose as little resistance as possible to the mechanical action of writing, but to resist the penetration of the ink in such a way that the written characters sink into the substance of the paper in the one direction only, i.e. normal to the surface.

These properties are in a large part *added* by means of *sizing agents*. While we shall consider the sizing process from this point of view, it must not be forgotten that the texture of the paper is an important factor, and that this is influenced by everything which tends to 'close' the sheet: for instance, the mineral loading agents (to be dealt with in the next section) have the effect of filling up the interspaces between the fibres: or the effect may be produced by suitable beating of the pulp. Thus, though the 'sizing' of paper may appear to be a simple process of adding substances of certain water-resisting quality, which quality they communicate to the paper, the experienced paper-maker recognises it as a really complicated result, influenced by a great number of factors. This is more particularly the case with the pulp or engine-sizing processes—which in the sequence of treatments will be considered here. The alternative method of sizing the finished sheet or web, 'tub-sizing,' as it is called, is a simpler process which in the case of machine-made papers is carried out on the paper-machine, and will be dealt with in that connection.

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Engine Sizing. (Rosin-alum-sizing.)—For the specific water- or ink-resisting quality specially required in writing and wrapping papers, we are practically limited to rosin or colophony. This well-known substance is the residue from turpentine distillation. It consists of an acid body, abietic acid ($C_{44}H_{64}O_5$), or rather of its anhydride ($C_{44}H_{62}O_4$). By virtue of its acid character and the solubility of the sodium salt ($C_{44}H_{62}O_5Na_2$) of the acid, rosin is rapidly dissolved on heating with solutions of the alkalis, e.g. carbonate of soda, caustic soda. The solution of the rosin-soap is similar in properties to solutions of the ordinary soaps, which are soda compounds of the higher fatty acids, and in fact the similarity of properties is such that mixtures of fat and resin acids, the latter in large proportion, are the basis of the 'yellow' soaps of commerce, which, but for the slight difference in colour and smell, are not distinguishable from fatty acid soaps.

The reaction between abietic acid and carbonate of soda, with expulsion of carbonic acid (gas), may be formulated as follows :—

$$\underset{[672]}{C_{44}H_{64}O_5} + \underset{[106]}{Na_2CO_3} = C_{44}H_{62}O_5, Na_2 + CO_2 + \underset{[\text{Beilstein}]}{H_2O} ;$$

that is, 100 parts of the pure acid require 15·7 of the pure carbonate to form, with the sodium oxide which it contains, the 'neutral' resinate. Commercial rosin being a mixture, and containing other acids which require more soda per unit, and, on the other hand, hydrocarbons and some other compounds devoid of acid properties, the 'equivalent' of soda (carbonate) will vary from 15 to 18 p.ct. with various rosins. The equivalent is readily determined for any sample by warming with excess of a standard solution of caustic soda in alcohol till completely dissolved, and titrating the excess of soda with a standard alcoholic acid in presence of phenolphthalein, as indicator (see p. 337).

To make the *neutral* rosin size on the large scale, the calculated quantity of soda ash is dissolved in about twelve times its weight of water, heated preferably in a jacketed pan : the

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rosin, previously crushed, is gradually added to an extent equal to about six times the weight of the ash, and the boiling is continued 3–4 hours until a perfect solution results.

The frothing due to the escape of large quantities of carbonic acid is controlled by the form of the boiling vessel, and by limiting the steam jacket to the lower portion, so that the sides are not superheated.

The boiling being finished, the strong 'size' is run off into iron tanks, where in cooling and standing a separation of the 'pure' soda resinate takes place as a semi-solid mass surrounded by a dark coloured liquor, which is a solution of various by-products.

In the older practice of size-making this solution was drained away and the size again boiled up with water. On cooling a further separation of coloured products takes place, with a consequent further purification of the 'size.' These operations requiring considerable time, it was customary to boil the supply of size many days in advance, the interval being required for the series of cleansing operations. The quantity of this size per 100 lb. paper is that representing 3–4 lb. of the original rosin.

In later practice, however, a rosin size is largely used, differing from the above in containing 15 to 25 p.ct. of rosin over and above the 'equivalent' of the soda, the excess of rosin being dissolved in the strong size in the free or uncombined state. For an *acid size* of this composition, finishing with 25 p.ct. of 'free rosin,' the following formula is given by C. Beadle: 170 lb. soda ash in 200 gallons of water are boiled with gradual addition of 1300 lb. rosin; the boiling is continued 7 hours, and the volume finally made up to 225 gallons. The acid size on dilution gives a milky liquid, due to suspension of the 'free' rosin in a finely divided condition. More care is required in diluting the size preparatory to adding to the beater, since with undissolved rosin there is a danger of agglomeration to particles of such dimensions as would cause rosin-specks in the paper. The danger is lessened by adding starch to the diluting water. The following working formula

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is given by Wurster (*infra*): In a suitable vessel water is heated to 50° C. A quantity of starch calculated to 15–20 p.ct. of the rosin in the size to be diluted, is stirred with warm water to a cream and added to the vessel, which is then heated to 80° until the starch is entirely 'dissolved.' The temperature is lowered to 50°–60° by adding water, and the strong size is then stirred in. Finally the temperature is gradually raised to 65°. The extent of dilution has a considerable effect on the efficiency of the size. Wurster recommends a 3 p.ct. limit, i.e. 3 lb. rosin per 10 gallons size.

Still more recently, acid sizes containing as much as 45 p.ct. of free rosin have come into use, the dilution of which without flocculation of the rosin is a matter of greater difficulty. This difficulty is, however, overcome by the use of 'atomisers' working on the injector principle, by means of which the strong size is mixed first with a small proportion of hot water, and then with a larger quantity of cold water.

The quantity of the acid size usually required is that representing 2–3 lb. of the original rosin per 100 lb. paper.

The sizing operation consists, *first*, in adding the size, prepared by either of the above methods, to the pulp in the beater, passing it through a fine sieve or a coarse cloth filter-bag. It is usually added when the pulp is one-half or two-thirds beaten. But following the addition of the size is a *second* operation by which the decomposition of the soda-resinate is determined, or perhaps rather completed, and the resin acids fixed upon the pulp in the insoluble condition. The reagent used for this purpose, almost universally, is alum or sulphate of alumina. In elucidating this reaction we must consider some of the properties of the alkali salts of the resin and fatty acids. These salts are easily decomposed by the weak acids, even carbonic acid, the action of which, expressed by the equation—

$$CO_2 + H_2O + C_{44}H_{62}O_5 . Na_2 = Na_2CO_3 + C_{44}H_{64}O_5,$$

is the exact reverse of that formulated on p. 207, and it takes place in dilute solution at the ordinary temperature. We

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note also that 44 parts of carbonic acid (CO_2) set free 682 parts of the resin acid. Other acids act similarly, and in proportion to their equivalents. Such acids, when combined with metallic bases, also pass over to the soda of the resinate, when the two salts are brought together in aqueous solution, with simultaneous formation of the resinate of the metallic base. Thus, with calcium salts,

$$\underset{\text{Calcium Chloride.}}{CaCl_2} + Na_2R = \underset{\text{R = Resin Acid.}}{Ca\,.\,R} + 2\,NaCl\,;$$

$$\underset{\text{Calcium Sulphate.}}{CaSO_4} + Na_2R = Ca\,.\,R + Na_2SO_4.$$

These reactions are all of practical significance: (1) because nearly all natural waters contain carbonic acid, and many contain the sulphate of lime; and (2) calcium chloride is contributed to the pulp by the bleaching solution, and is present in the beater, less or more, according to the degree of washing of the pulp after bleaching. These resinates are curdy insoluble precipitates. Sulphate of alumina reacts according to the equation—

$$3\,.\,Na_2R + Al_2\,.\,3SO_4 = 3Na_2SO_4 + Al_2R_3\,;$$

i.e. for 3 mol. abietic acid (= 2016) in a *neutral size*, we require 342·8 of the *sulphate*; or in terms of alum, which contains 36·1 p.ct. sulphate of alumina, 949 parts. In the acid sizes, the proportion of soda being less, and in the sulphates of alumina of commerce, the proportion of Al_23SO_4 varying from 40 to 60 p.ct., it is necessary in every mill to construct a table of 'alum' equivalents for the size, according to the composition of each. Thus, as an example, the size is made with 15 p.ct. soda ash per 100 lb. rosin, and the sulphate of alumina to be used contains 50 p.ct. Al_23SO_4. The 'alum equivalent' per 100 lb. rosin is

$$\frac{342\cdot8}{2} \div 106 \times 15 = 23 \text{ lb.},$$

or 0·23 sulphate per 1 lb. rosin.

As a matter of fact, however, the quantity used in practice

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is much in excess of this proportion—usually about three times, but often very much more. This 'optimum' proportion has been determined rather by experience than by quantitative calculations based upon scientific grounds. In 1878, C. Wurster published a treatise on the Rosin-Alum Sizing Process,* which may be regarded as the first attempt to reduce the process to a scientific or exact basis. Wurster combats the then current view that the actual sizing agent is a resinate of alumina formed as above represented. It appears that ordinary engine-sized papers treated with ether and other solvents of the *resin acids*, entirely lose their water-resisting quality, losing in weight from 2 to 5 p.ct.; these dissolved sizing components are isolated by evaporation of the solvent, and found to be almost entirely composed of the *free resin acids*. This observation is also confirmed by determining the alumina in the paper before and after extraction; which is found to be but slightly affected. On these results Wurster concludes that the free rosin acids are the effective sizing agents, and hence his advocacy of the acid sizes with a maximum proportion of free or uncombined rosin; hence also the function of the excess of alum, i.e. to decompose the neutral resinate of alumina with liberation of the free acid, thus:—

$$Al_2R_3 + 2Al_2(SO_4)_3 + 3H_2O = 3R.H_2 + 3Al_2O(SO_4)_2.$$

Free Resin Acid. Basic Sulphate of Alumina.

These views require complementing by a careful consideration of the chemical function of the *cellulose itself*. It is well known that cellulose takes up alumina from solutions of the sulphate and chloride; still more easily from the acetate. It is, therefore, more than probable that cellulose would decompose the neutral resinate by combining with the alumina. It must also be borne in mind that cellulose contains OH-groups of basic function, and that these would combine simultaneously with the rosin acids; nor is this view negatived by the fact that ether and other solvents dissolve away the rosin acids from the finished paper.

* 'Le Collage des Papiers,' Bull. Soc. Ind. Mulhouse, 1878, pp. 726–801.

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On the whole, therefore, it is to be recommended that all these contributing factors should be borne in mind: (1) the consumption of alum by the basic constituents of the cellulose half-stuff and of the water used in furnishing; (2) the calculated proportion referred to the soda used in the particular type of rosin size adopted; (3) the proportion required by the cellulose itself. For a further discussion of this somewhat complicated problem, see 'Society of Arts Journal' (Cantor Lectures), Feb. 22, 1897.

Experience has shown that the best results for hard-sized writing-papers are obtained when the finished paper possesses a slightly acid reaction to litmus solution. If the contents of the beating engine be gauged either by volume or according to the weight of dry half-stuff in the furnish, the minimum quantity of alum required to neutralise the basic constituents of the pulp can be readily determined by titrating a measured portion of the stuff with standard solution of alum in presence of litmus as an indicator.

In many mills it is customary to add a portion of the alum to the beater before running in the diluted size. This procedure has the justification of practical survival, although it is probable that the interaction between the rosin and the fibres is not so intimate as when the size is added first. But the prior addition of alum, owing to the superior acidity of that salt, prevents the 'curdling' of the rosin by the soluble calcium salts present in the pulp; it also prevents undue frothing and the precipitation of calcium carbonate in the pulp, which if allowed to accumulate might produce 'soft-sized' spots in the paper.

It should be mentioned that the sizing of the paper is not complete until the web has passed over the hot drying cylinders, under the action of which the precipitated particles of rosin fuse together and form an impervious film over the surface of the individual fibres.

Auxiliary Sizing Agents.—Under this heading we may mention certain colloidal substances which are or may be used in the engine-sizing process, chiefly for the purpose of closing

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and compacting the web of fibres. Two of these we have already had occasion to introduce to notice, viz. *Starch* and *Alumina*.

Starch is used by many makers in large proportion, especially in papers heavily 'loaded' with china clay (p. 220). It is sometimes added in the form of transparent starch paste, prepared by swelling and dissolving the starch at 80°–90°; it is a common practice also to boil the clay with its complement of starch. In many mills, again, the starch is added in the raw or unswollen state, the granules become imprisoned in the network of fibres, and are swollen and burst under the heat of the drying cylinders. In such cases, however, a considerable proportion is carried away in the backwaters.

Alumina is precipitated as a gelatinous hydrate by the basic constituents of the water and by the interaction of the rosin size with sulphate of alumina.

Passing through the intermediate form of 'resinate,' it is no doubt finally fixed as the oxide, and aids in cementing the fibres together and filling the interspaces. Both the alumina and starch also aid in keeping the rosin acids in the state of minute subdivision during the beating and making processes.

Soap.—Solutions of ordinary 'curd' soaps, free from rosin, are sometimes added to the beaters in the same manner as rosin-size, and are precipitated in the pulp by means of alum. The effect of these soaps is not a real 'sizing' but they certainly increase the ink-bearing qualities, particularly the resistance, after erasure, of papers which are subsequently tub-sized. The soft 'waxy' character of the alumina soaps thus precipitated in the paper appears to assist the cohesion of the fibres under the action of pressure, and to improve the surface and texture of the finished sheet.

Cellulose Hydrates (*'Viscose' Sizing*).—In the earlier part of this work attention has been called to the specific charateristics of the celluloses of parenchymatous or 'cellular' as distinguished from fibrous tissue. Under chemical treatment these are gelatinised to hydrated forms which retain a rela-

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tively large percentage of water. Such forms of cellulose no doubt play an important part in paper-making. Certainly the special characteristics of straw cellulose are largely due to the presence of such 'cellular' celluloses, and also to the general capacity for hydration of its constituent celluloses. The various solutions of cellulose dealt with in Chapter I. would appear to be available for a similar purpose, but for practical use they are mostly precluded by cost of production.

The sulpho-carbonates, however, being prepared at relatively low cost, and readily decomposed with regeneration of a normal cellulose endowed with powerful cementing properties, are successfully used in engine sizing. The solution, which goes by the name of 'viscose,' is added to the beater in the earlier stages of the beating, and when thoroughly mixed the decomposing salt is added. The salts best adapted to this purpose are the sulphates of zinc and magnesium, the proportion required being calculated to the equivalent of the soda present in the viscose. Thus, as an example, the wood celluloses are converted into 'viscose' with a proportion of caustic soda (NaOH) equal to 40 p.ct. of the weight of the cellulose. The molecular weight of NaOH being 40, and its equivalent of the salts being respectively

$$\frac{ZnSO_4.7H_2O = 287}{2}, \text{ i.e. } 143{\cdot}5$$

and

$$\frac{MgSO_4.7H_2O = 246}{2}, \text{ i.e. } 123{\cdot}0$$

each lb. of dissolved cellulose will require nearly 1½ lb. of the zinc and 1¼ lb. of the magnesium salt.

The decomposition of the viscose has the effect of coating the fibres with a film of gelatinous cellulose, which exerts a powerful cementing action in the subsequent processes of making and drying, the effects reaching a maximum when the paper is 'loft dried,' i.e. dried in the air without heat. By viscose sizing the contents of the beater are still left in the basic condition, and it is necessary to add alum in slight excess

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in order to facilitate the working on the machine. The quantity of viscose used is usually from 1 to 5 p.ct. (calculated as dissolved cellulose) of the weight of the paper. The effects produced are a considerable increase of tensile strength and resistance to the action of water, though the sizing in the latter respect is not of the character of rosin sizing. To produce the quality of resistance to penetration by water and ink the addition of rosin is necessary. It is found, however, that very much less of the latter is required, viz. from $\frac{1}{2}$ to $\frac{1}{3}$ the usual quantity, or 1 to 2 p.ct. on the paper. These advantages of the viscose or cellulose sizing are realised at only a small additional cost to that of the ordinary plan; but certain disadvantages have to be reckoned with, resulting from the introduction of alkaline sulphur compounds into the beater. These, by interaction with the fibre constituents, and also by action upon iron compounds unavoidably present, cause a certain lowering of colour; and although the sulphur introduced is for the most part eliminated (as CS_2) by the special action of the decomposing salts, and the alkalinity is of course easily neutralised by alum, there is a residual permanent discoloration sufficiently marked to prevent the process being used in the ordinary production of white papers.

Aluminate of Soda has been used to a certain extent as a sizing agent in conjunction with the rosin-soap. Hydrated alumina dissolves in caustic soda by virtue of its acid function—a characteristic which it is important to bear in mind in considering the probable chemical condition of the oxide in the finished paper. The alumina is precipitated from its alkaline solution by the weakest acids, e.g. carbonic acid—and therefore *à fortiori* by alum itself. It has been proposed to use the aluminate of soda as the solvent for the rosin; but it is difficult to see any advantage resulting from the practice.

The addition of hydrated alumina to the neutral rosin-size during the later stages of the boiling, is rather to be recommended.

Silicate of Soda.—Silica, or SiO_2, is a solid body of weakly acid properties, which is precipitated from solutions of its

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alkaline salts on the addition of acids and acid salts. It takes the form of a gelatinous hydrate, which, when formed in the beater, enables the pulp to carry more water in the machine, and produces a hardening effect on the paper. In using this compound the more 'acid' silicates should be selected, e.g. the silicates of formula $Na_2O \cdot 2SiO_2$, $Na_2O \cdot 3SiO_2$.

Gelatin is little used in engine-sizing. Used in this way it fails to give results proportional to cost. Its compound with the sulphonated lignone derivatives, the by-products of the bisulphite processes, has been already mentioned. It is soluble in weak alkaline solutions, in which form it is added to the beater, and on being decomposed with the equivalent of alum is reprecipitated as a tough caoutchouc-like mass, which, as a coating upon the fibres, produces a considerable toughening effect upon the paper.

Casein.—This albuminoid substance, obtained from milk—of which it constitutes nearly 5 p.ct. by weight—is largely used as a sizing agent in the coating of papers. Its use in the engine depends upon the fact that it can be added in the form of a strong solution from which it is completely precipitated by alum. It imparts toughness and a good 'handle' to the finished paper. Its use has been limited by cost, but at present rates, viz. between $2\frac{1}{2}d.$ and $3d.$ per lb., the consumption for this purpose is increasing.

Particulars of Materials used in Sizing.

The following are the more important points which determine the value of the materials, their preferential selection, mode of use, etc.

Soda (*Carbonate*) occurs commercially in various forms:—

Crystal Soda ($\underset{106}{Na_2CO_3}\underset{180}{10H_2O}$) is the ordinary 'washing soda.' From the formula it is seen to contain $\frac{106}{286} \times 100 =$ 37 p.ct. only of the carbonate, the remainder being water. It is therefore a relatively costly form of soda to handle.

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Crystal Monohydrate ($Na_2CO_3 . H_2O$) was introduced many years ago by Messrs. Gaskell, Deacon and Co. It has one point of advantage over the anhydrous carbonate or soda ash, viz. that it dissolves readily without tending to aggregate to lumps.

Soda Ash (Na_2CO_3, anhydrous and nearly pure).—Before the introduction of the Solvay process and the so-called 'ammonia' soda, soda ash was an impure form of the carbonate. The degree of impurity was such that the percentage of carbonate in the ordinary forms varied from 83 to 90. Such products were objectionable for use in the making of size. Now, however, we have in the aforesaid 'ammonia' soda a remarkably pure product, the percentage of carbonate amounting to 97–98. This answers all requirements for size making.

Solutions of Sodium Carbonate.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE, At 60° F. = 15° C.

Degrees Twad. 1° = 0·005 Sp. Gr.	Percentage by Weight.		Degrees Twad. 1° = 0·005 Sp. Gr.	Percentage by Weight.	
	Na_2O.	Na_2CO_3.		Na_2O.	Na_2CO_3.
1	0·28	0·47	16	4·42	7·57
2	0·56	0·95	17	4·70	8·04
3	0·84	1·42	18	4·97	8·51
4	1·11	1·90	19	5·24	8·97
5	1·39	2·38	20	5·52	9·43
6	1·67	2·85	21	5·79	9·90
7	1·95	3·33	22	6·06	10·37
8	2·22	3·80	23	6·33	10·83
9	2·50	4·28	24	6·61	11·30
10	2·78	4·76	25	6·88	11·76
11	3·06	5·23	26	7·15	12·23
12	3·34	5·71	27	7·42	12·70
13	3·61	6·17	28	7·70	13·16
14	3·83	6·64	29	7·97	13·63
15	4·16	7·10	30	8·24	14·09

Alum : Sulphate of Alumina.—The basis of the alums is the *normal aluminium sulphate* Al_23SO_4; the pure sulphate in solution is acid to litmus.

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*Solutions of Aluminic Sulphate.**—The solubility of the anhydrous sulphate ($Al_2.3SO_4$) in water has been determined as follows :—

Temperature 0° C.	0°	10°	20°	30°	45°	50°
100 parts water dissolve of $Al_2.3SO_4$ . . .	31·3	33·5	36·2	40·4	45·7	52·1

The following are the specific gravities at 15° of solutions of varying concentration :—

Per cent. $Al_2.3SO_4$.	5	10	15	20	25
Specific gravity . . .	1·0569	1·1071	1·1574	1·2074	1·2572

Crystal Alum ($Al_2.K_2.4SO_4 + 24H_2O$) is a double salt of aluminium and potassium sulphates, the latter being inert and serving only for procuring a ready crystallisation of the sulphate of alumina. Of this, the 'active' sulphate, the double salt contains 36·1 p.ct. The double salt may be regarded as a pure but diluted form of sulphate of alumina. It is still used in certain mills, but is for the most part superseded by the 'alum cakes.'

Ammonia alum $Al_2 (NH_4)_2 4SO_4 + 24H_2O$ which is rather less soluble than potash alum, is also used.

The following is a table of strengths of potash alum solution at 17° C :—

Percentage of $Al_2K_2(SO_4)_4.24H_2O$.	Specific Gravity.	Degrees Twad.
1	1·0065	1·3
2	1·0110	2·2
3	1·0166	3·3
4	1·0218	4·4
5	1·0269	5·4
6	1·0320	6·4

Alum Cakes.—Many years ago an aluminous cake or 'concentrated alum' was introduced into the English paper trade by Messrs. Pochin. Such products have now almost entirely dis-

* Dic. Chem. Sol., A. M. Coney. London, 1896, Macmillan.

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placed the crystal alums. They are made by the action of sulphuric acid upon bauxite or iron-free clays. The subjoined analyses of commercial products show the standard of purity to which they now attain :— .

Alumina (Al_2O_3) . .	14·84	14·70	14·95	14·85	16·00	16·20
Ferric Oxide (Fe_2O_3) .	·06	·12	·05	trace	nil	trace
Sulphuric acid (SO_3) .	35·00	34·60	36·09	34·94	38·00	38·00
Free sulphuric acid .	·32	·40	nil	·29	nil	nil
Lime (CaO) . . .	·11	·11	·17	·14	·16	·14
Water	49·42	49·95	48·72	49·60	45·50	45·43
	99·75	99·88	99·98	99·82	99·66	99·77

These forms of the sulphate of alumina have certain advantages over the crystal alums : (1) in 'concentration' or percentage contents of the sulphate ; and (2) in being much more readily soluble in water ; the sulphate, in fact, is soluble in twice its weight of cold water, whereas potash alum requires 18 parts for complete solution.

In addition to the purer forms of the sulphate there are a number of products in the market containing more or less of insoluble matters representing residues of the original or aluminous mineral not attacked by the sulphuric acid.

The amount of alum or sulphate of alumina added to a pulp is largely in excess of the quantity necessary to precipitate the rosin soap : as a matter of fact, in the case of esparto or straw pulps, for the bleaching of which considerable quantities of bleach have been employed, and which therefore contain a certain amount of basic lime, together with calcium chloride, complete precipitation of the size is effected without the addition of alum. A certain amount is also required to precipitate the starch. The excess of alum appears to be necessary, however, not only to brighten the colour of the paper, but also to render it capable of resisting the action of ink. From experiments made by the authors, it appears that one part of rosin requires 2·9 parts of alum for complete precipitation from its solution in soda. One part of starch requires 0·40 part alum.

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Mineral Filling and Loading Agents.—It is usual, except in the case of papers of the very highest quality, to add to the pulp a quantity of some relatively cheap mineral loading material, such as china clay, or for certain qualities of paper, 'pearl-hardening,' or sulphate of lime. The addition of clay in moderate quantity can hardly be looked upon as an adulteration, since it serves to fill up the pores of the paper, thus giving a sheet of closer texture, with a smoother surface and more absorbent of printers' ink, and also enables it to take an improved surface in the subsequent operations of calendering. It also adds to the opacity of the paper—a very important point in book papers. Moreover, it enables the manufacturer to meet the demand for cheap papers. If added largely, it of course tends to weaken the paper.

China clay, or kaolin (Fig. 43), is sold in the form of large lumps of a white or yellowish-white colour. It is formed by the gradual disintegration of felspar under the action of air and water, and consists essentially of a silicate of aluminium. Its quality depends upon its whiteness, and its freedom from the coarser micaceous particles. It is usually prepared for admixture with the pulp by making it into a fine cream with water in a vessel provided with stirrers; it is then passed through a fine sieve in order to remove any impurities it may contain, and is then run into the beater. The clay or other filling material is usually run into the beater as soon as the latter is charged with pulp, so that by the time the beating operation is concluded a perfect admixture of pulp and clay is effected.

Sulphate of lime, or 'pearl-hardening,' is usually sufficiently pure to put direct into the engine. It is made by decomposing a solution of calcium chloride with sulphate of soda, and is precipitated as a fine brilliantly white powder, consisting of $CaSO_4 + 2H_2O$.

Two distinct forms of precipitated calcium sulphate are met with in commerce, differing from each other by their microscopical features, the one consisting of flat tabular crystals (Fig. 44), the other of fine needles (Fig. 45). Another form, erroneously called 'precipitated pearl-hardening,' is also sold:

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it consists of the finely ground native mineral. The use of these sulphates is attended by the disadvantage of their solubility

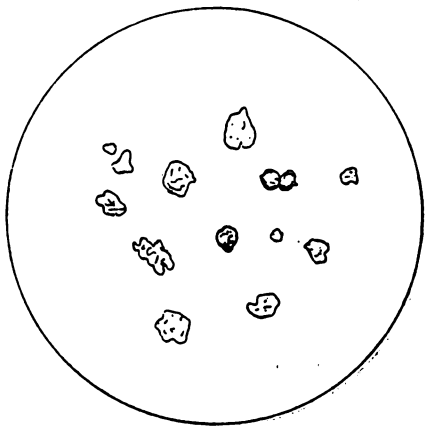

FIG. 43.

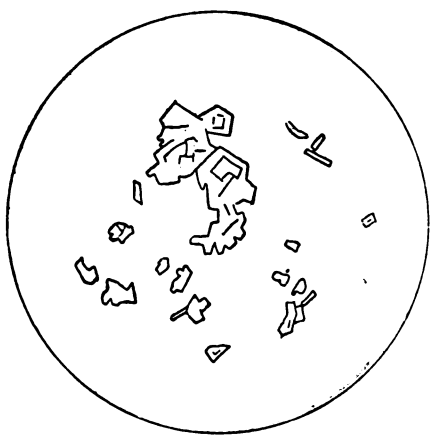

FIG. 44.

in water—which occasions loss on the machine. This is, of course, minimised in long runs on the machine, when the 'back water' becomes saturated with the sulphate.

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Some of the finer qualities of paper are made without addition of any loading material whatever, though such papers

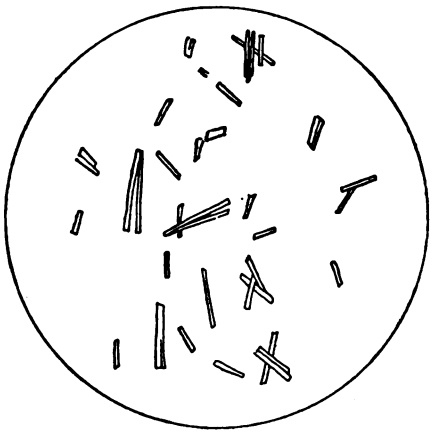

FIG. 45.

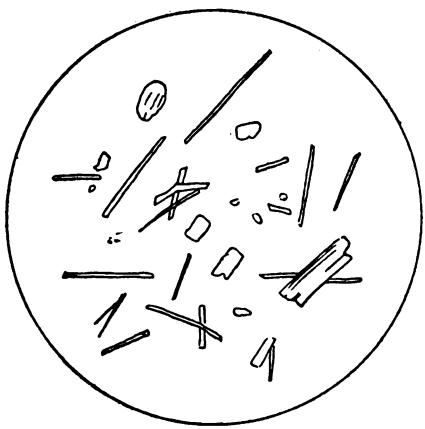

FIG. 46.

are of course the exception. The proportion of clay or other material that can be retained by a fibre depends to a certain extent upon the nature of the fibre, and upon the degree of

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fineness to which it is reduced in the beater. The amount added by different makers varies considerably, from 2 or 3 p.ct. to 20, and even in rare cases to 30, p.ct.

Other mineral filling agents having a certain fibrous character have been from time to time introduced, possessing certain advantages over china clay or calcium sulphate. Agalite (Fig. 46) is a mineral of the nature and chemical properties of asbestos: it consists of nearly pure magnesium silicate. Its structure is more or less fibrous, like that of asbestos, which, as is well known, can be spun and woven, and even made into paper, and therefore, when added to a paper, it forms a part of the fabric itself. It is even claimed that it assists in keeping back some of the finer fibres that invariably find their way through the meshes of the wire-cloth, and it is said that 90 p.ct. of the amount added to the engine is found in the paper. In the case of china clay it is well known that only from 40 to 60 p.ct. is often actually 'carried' by the pulp. Figs. 43, 44, 45 and 46 show the appearance of china clay, pearl-hardening and agalite when viewed under the microscope, magnified 200 times. The nature of agalite is such that it assists the paper in taking a high finish. This is probably due to its 'soapy' nature, a feature which is characteristic of asbestos, French chalk, 'soapstone,' and other magnesium silicates.

The following analysis of china clays may be cited :—

Alumina	39·74	33·44
Iron oxide	0·27	1·04
Calcium	0·36	1·01
Magnesium	0·44	0·16
Silica	46·32	42·72
Water	12·67	20·93

Sp. gr. varying from 2·5 to 2·8.

The following is an analysis of 'agalite' :—

Magnesia	32·12	30·70
Iron oxide	0·10	—
Alumina	0·31	—
Silica	62·01	61·90
Water	4·30	—

Sp. gr. varying from 2·6 to 2·8.

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When papers contain such excessive quantities as 15 or 20 p.ct. of clay, it cannot be to the advantage of the consumer, and should be looked upon as an adulteration.

Analytical Determination of Loading.

It is a matter of some importance to be able to determine rapidly and accurately the amount of mineral matter in a paper. The usual method is to ignite a weighed quantity of the paper in a platinum crucible until the ash so obtained is either white or a very pale grey. From the weight of the ash, the percentage of mineral matter is easily calculated.

In certain cases it may be necessary to take into account both the normal ash of the paper and that due to other added mineral matter. This requires an analytical investigation of the total ash obtained, and a careful interpretation of the results. We can only note here that the processes of treatment add chiefly *lime salts*, which are obtained in the ash mainly in the form of carbonate. A correction is also necessary for the water chemically combined with the mineral, and expelled on ignition.

The ignition may be performed in an open platinum dish, and to hasten the complete combustion of the carbonaceous residues the dish should be covered with a piece of platinum foil, bent in the middle to allow free access of air.

A cage of platinum gauze or a closely wound spiral of platinum wire is sometimes substituted for the dish or crucible.

The weighings may be performed upon any balance of sufficient delicacy for the degree of accuracy required. A spiral balance of the form devised by Joly, and fully described in the First Edition of this book, is a convenient instrument for rapid work.

In brown and coloured papers, various *coloured mineral loading agents* are used; thus the ochres, which are chiefly oxides of iron, chrome yellows, chiefly chromate of lead.

Ultramarine in heavy blue papers is used in sufficient quantity to have a certain 'filling' effect.

These substances or their products of decomposition are

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obtained in the ash. If clays or other loading agents are also present, the proportion of pigment-loading may be approximately estimated by separating its characteristic constituent by suitable analytical treatment of the ash.

If the paper contains calcium sulphate, the ash obtained may consist partly of calcium sulphide, due to reducing action of the carbon found on ignition, and the amount will therefore not represent the true amount added. The ash should be moistened with a few drops of sulphuric acid, and again ignited, in order to reconvert it into calcium sulphate. It should also be borne in mind that the sulphate of lime as present in the paper is combined with two atoms of water $CaSO_4 + 2H_2O$, and therefore that every part of calcium sulphate obtained represents 1·26 parts of 'pearl-hardening' actually in the paper.

China clay also contains variable proportions of chemically combined water, for which allowance should be made. Analyses of typical samples will be found on p. 223.

Colouring.—The colouring of paper in the paper-mill is effected by the addition of pigments or solutions of dyestuffs to the pulp in the beater. Colouring with pigments is, of course, a purely mechanical operation. At the same time it must be remembered that many of the paper-makers' pigments are reactive chemical compounds, and when acted upon by substances present in the beater, e.g. rosin-size and alum, may be destroyed or modified, with attendant loss of colour or alteration of shade. Attention must be paid, therefore, to the chemical composition of pigments, in order that their full colouring power may be realised and permanently retained in the paper. The soluble dyes are for the most part artificial products of well-defined chemical constitution. An intelligent application of these products by the paper-maker presupposes an intimate knowledge of the general principles of the dyer's art. We may note, however, at this point, that the makers of coloured papers are comparatively few; whereas, on the other hand, there are few papers made which do not receive some addition of colouring matter. Thus all bleached pulps retain

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a residual yellow tint more or less pronounced, and for white papers the yellow requires to be 'neutralised' or 'corrected' by the addition of blue and red, producing a 'neutral' or dyed white. In effect these dyed whites are greys, but the balance or neutralisation of colour produces an illusive impression of whiteness. In view of their more general importance we shall deal first with colouring matters and methods used in producing these dyed whites.

1. The following are the more important colouring matters :—

BLUES.—*Ultramarines* of various shades, tending on the one side to red, on the other to green tones of blue. The modern ultramarines are artificial products consisting essentially of silica, alumina, soda and sulphur, and are prepared by fusing together mixtures of raw materials furnishing these components. The coloured body itself may be regarded as a sodio-aluminic silicate, united either with a polysulphide of sodium or with a polysulphide and polythionate.

The former relationships are expressed by the formula :—

$$2Na_2Al_2Si_2O_8 . Na_2S_2.$$
(Heumann)

The compound is attacked by the mineral acids, or even by hot solutions of alum, hydrogen sulphide being liberated ; it is also rapidly attacked by chlorine and oxides of chlorine. The decomposition is synonymous with destruction of colour.

The degree of resistance to the action of sulphate of alumina is found to depend upon the proportion of silica in combination : ultramarines 'rich in silica' (SiO_2 = 40·7 p.ct.) are resistant ; those 'poor in silica' (SiO_2 = 37·9 p.ct.) are decolorised by a cold solution of alum.

Smalts.—This is a pure blue pigment obtained by reducing a cobalt-glass to the finest state of division. The glass is essentially a potassio-cobaltous silicate,

$$K_2O . CoO . 6SiO_2,$$

with varying proportions of alumina and iron oxide as incidental impurities. The deep-coloured varieties contain

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6–7 p.ct. CoO; 70–72 p.ct. SiO_2; 17–21 K_2O (with Na_2O). This pigment is extremely permanent and resistant to chemical action. On account of its high price it is used only in papers of the highest quality.

Soluble Dye-Stuffs.—The blues and violets used in tinting for whites are chiefly 'aniline' derivatives. The 'soluble blues' are the sulphonic acids of phenylated rosanilines. The 'methyl violets' are methylated rosanilines. The induline class of blues are greyish blues of various tones, obtained as by-products in the manufacture of rosaniline. They are oxidation products of aniline. This group includes the nigrosines, Blackley blue, etc.

Methylene blue is a useful fast blue, of pure tone, and is obtained from dimethyl-paraphenylene-diamine by the action of sulphides and subsequent oxidation. It contains sulphur as an essential component.

REDS, of the pigment or lake class, are seldom used in tinting for whites.

Soluble Dye-Stuffs.—Of these one of the most important is the colouring matter of the cochineal insect. From the raw product a dye liquor may be prepared, either by exhaustion with boiling water or by long steeping of the material with strong aqueous ammonia in a closed vessel. The latter is the more convenient method. After steeping, the mass is thrown on to a conical flannel bag, which is then suspended in a vessel of water. By diffusion, followed by squeezing and washing, the exhaustion of the colour is completed. 5 lb. of material treated in this way will make 10 gallons of 'cochineal liquor' of ordinary working strength.

Of the coal-tar dyes, the paper-maker uses (1) of the rosaniline group, the various magentas; (2) the safranines which are poly-aniline derivatives; (3) azo-dyes, derived from benzidine, especially benzo-purpurine; (4) the eosines, which differ essentially from the three preceding groups in containing no nitrogen: they are derivatives of the coal-tar phenol resorcin, and not of nitrogenous bases; (5) rhodamine, a basic nitrogenous dye-stuff of the same group: a fairly fast and very useful pink.

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Applications.—The use of the above colouring matters in white papers involves, for obvious reasons, very small proportions. Of the blue pigments an average proportion is 0·1 p.ct. of the weight of the 'furnish'; of cochineal 0·01–0·02 p.ct., calculated as original cochineal per 100 lb. furnish. The coal-tar dyes, having greater tinctorial power, are used in still less proportion. There are no general rules which can be laid down as to the stage in the beating process when the colour should be added. Where, however, the colouring matter is not affected by the rosin-size, it is better to add it while the contents of the beater are alkaline from its addition. The soluble dyes should not be added in the form of the ordinary stock solution, which may contain from 2 to 5 p.ct. of the dissolved dye-stuff. This should be diluted considerably before adding to the beater, and well distributed in adding it.

2. *Coloured papers*, as distinguished from whites—which are dyed whites—and self-coloured papers are produced with larger proportions of colouring matters. To those used in tinting for whites we have to add other blues, and reds, and also those giving yellows and browns, and also greens. The following are the more important:—

Prussian blues of various grades. These are the ferroso-ferric ferrocyanides formed by decomposing a mixture of ferrous and ferric salt in solution, with a soluble ferrocyanide. These blues are sold in paste form, under various trade names. They are recognised by being at once decolorised by the caustic alkalis, the basic iron oxide being left as a brown residue.

These blues are often formed by bringing together the above-mentioned salts in the beater, i.e. a mixture of ferrous and ferric sulphates (copperas and 'red iron liquor') added first and followed by the equivalent quantity of potassium ferrocyanide (yellow prussiate). Dyeing with Prussian blue in this way is carried out after the sizing operations are complete. It may be noted here that all paper 'furnishes' contain iron compounds as an impurity, in greater or less degree, and in some cases this is taken advantage of for conversion into the

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blue ferrocyanides by addition of the potassium salts to the beater in correspondingly small proportion.

Logwood.—The aqueous decoction, or the concentrated extracts sold in the trade, are used in producing the darker shades of blue, usually in admixture with Prussian blue; also for a larger number of heavy mixed shades and for blacks.

Alizarin (madder).—This most important red dye is not used directly in colouring papers. It occurs in the form of pigments or insoluble lakes, which are compounds of the colouring matter with alumina, etc.

Alizarin printed cottons and 'Turkey red' rags may be beaten after the alkali treatment to a coloured pulp.

Iron oxide pigments cover a wide range of gradations of colour from the reds (rouge) to browns (the umbers, containing also manganese), and from these to the yellows of the 'yellow ochres.'

Yellows.—Of the pigment class the most important is the brilliant chromate of lead. This is usually formed in the beater by the interaction of lead acetate and the alkaline bichromates.

Of coal-tar dyes the more important yellows are Auramine, a basic dye-stuff, a derivative of dimethyl-aniline; naphthol yellow, which is the alkali salt of di-nitro-naphthalene; primuline, a sulphur-containing derivative of toludine; and a large number of azo and amido-azo derivatives, such as metanil yellow, the tropæolins, chrysoidines.

Greens.—The mineral green pigments are but little used by the paper-maker. Mixtures of blue and yellow pigments, e.g. Prussian blue and lead chromate, are however employed. The more important coal-tar dyes are malachite green, a derivative of rosaniline, and 'acid' greens, which are the sulphonic acids of the group of the 'malachite' or benzaldehyde greens.

Browns.—In dyed browns the paper-maker uses a number of pigments of the iron and manganese group.

Of soluble dye-stuffs an important group is furnished by the 'natural' astringents, or tannin derivatives, e.g. catechu and gambir. The catechu liquor is prepared by boiling the

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finely powdered raw material for 2–3 hours with 3–5 times its weight of water. When cold a solution of sulphate of copper, calculated to 6 p.ct. of the weight of the catechu, is added. In using these tannin colouring matters, bichromate of soda is used to develop or intensify the brown, iron salts for deepening or blackening the shades.

A medium brown is obtained with 4 p.ct. catechu on the furnish 'developed' with one-sixth its weight of the bichromate. Of coal-tar dyes there are a large number of browns. The well-known Bismarck browns are salts of tri-amido-azobenzene.

Applications.—The dyeing of paper pulps in the engine is an art which can only be said to be grasped when the whole of the factors involved are intelligently followed. To do this it is necessary to take into account all that has been advanced in the earlier chapters as to the constitution of the celluloses, their general inertness, accompanied by graduations in chemical reactivity such as obviously affect their relationships to colouring matters, the combination with which is undoubtedly a chemical phenomenon. Therefore also the constitution of the colouring matters themselves must be taken into account. Lastly, owing to the inertness of the celluloses and more especially those of the cotton group, the cotton dyer is limited to comparatively few dyes or groups of dyes which combine directly with the fibre: in the majority of his processes he requires the assistance of intermediary substances known as *mordants*—compounds which combine directly with the fibre-substance *and* the colouring matter, and which therefore in combination with the former enable it to take up and fix the colour in the insoluble condition.

Owing to the development of the industry in coal-tar colours, and the enterprise of manufacturers, the paper-maker is certainly saved much trouble by being supplied not only with a practically infinite range of colours, but with working specifications of methods of using them, including particulars as to the mordants required. In view of this extensive specialisation, we make no attempt to treat the subject in detail.

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The student must be referred to such special treatises as the following :—

(1) On the general principles of dyeing ; 'The Dyeing of Textile Fabrics,' by J. J. Hummel (London, Cassell and Co.).

(2) On the constitution of the colouring matters : 'The Chemistry of the Coal Tar Colours,' by Benedikt and Knecht (London, G. Bell and Sons).

(3) For working formulæ for the colouring of pulp in the engine, those contained in J. Dunbar's 'The Practical Paper-Maker' (London, 1887, Spon) are useful and typical of a wide range of effects.

(4) 'Dyeing of Paper Pulp,' J. Erfurt (translated by J. Hübner). (London, Scott Greenwood and Co.).

The paper colourist may either work on purely empirical lines, i.e. by means of recipes and specifications supplied to him ; or he may by his own investigations devise endless combinations to produce special effects, or produce the usual effects by specially economical means. In either case it may be pointed out that since uniformity is of the utmost importance, all conditions of preparation and treatment must be kept rigidly uniform.

In matching colours, allowance must be made for the condition of the stuff in the beater, and alterations of shade which take place during the process of making into paper—(1) by incidental variations in the composition of the backwater in the machine ; and (2) by the action of the heat of the drying cylinder. The usual practice of matching is to make up a sheet of paper in a hand-mould from the stuff in the beaters, which is then pressed and dried on a hot cylinder or steam pipe. The examination of the colour by comparison with the sample requires care and attention. A good 'white' light must be chosen, preferably daylight in a north aspect. Matching at night requires that the artificial light shall be of exceptional purity.

During the time that the loading, sizing and colouring processes have been going on, the pulp has been continually

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acted upon by the roll, and if these operations have extended over a considerable time, it is probably in a proper condition for making into paper. The amount of 'beating' depends, as has been stated before, upon the nature of the fibre, and also to some extent on the nature of the paper for which it is intended. The 'beater-man' examines the pulp from time to time by taking a portion from the engine and placing it in a hand-bowl containing water: from its appearance when so diluted he is able to judge of the time during which it may be necessary to continue the disintegration. As soon as this is completed, the pulp is ready to be let down to the stuff-chests, usually placed at a lower level than the beaters, so that the pulp can flow into them by gravity. For this purpose the valve at the bottom of the engine is opened; to remove the last portion of pulp it is necessary to rinse out the engine with water.

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CHAPTER IX.

PAPER MACHINES; HAND-MADE PAPER.

THE pulp as it comes from the beaters is now ready to be made into paper. We will first consider briefly the manufacture of hand-made paper.

It is made on a mould of wire-cloth, with a movable frame of wood, called the 'deckle,' fitting on to the outside of the mould, and extending slightly above its surface.

The wire-cloth is generally supported by a much coarser wire-cloth, or by pieces of thick wire, and these again by wedge-shaped pieces of wood, the thin end being next to the wire.

To form a sheet of paper the workman dips the mould with the 'deckle' in position, into a vat containing the prepared pulp diluted with water, lifting up just so much as will make a sheet of the necessary thickness. As soon as the mould is removed from the vat, the water begins to drain through the wire-cloth, and to leave the fibres on the surface in the form of a coherent sheet. The felting or intertwining is assisted by lateral motion in every direction given to the frame by the workman. The movable deckle is then removed, and the mould, with the sheet of paper, given to another workman, called the 'coucher,' who turns it over and presses it against the felt, by this means transferring the sheet from the wire to the felt. In the meantime the 'vat-man' is engaged in the formation of another sheet with a second mould.

A number of the sheets thus formed are piled together, alternately with pieces of felt, and when a sufficient number has been obtained, the whole is subjected to strong pressure to expel the water. The sheets of paper are then removed from the

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felts by the 'layer,' and the sheets are again pressed as 'packs' and hung up to dry.

They are then sized, if required, by dipping them into a solution of gelatine: again slightly pressed, and hung up on lines or poles to dry. Such paper is called loft-dried.

When dry the sheets of paper are calendered (see Chapter X.), plate-glazed, or otherwise finished.

The making of paper by hand involves considerable dexterity on the part of the workman; on account of the expensive labour necessary, in comparison with paper-machines, it is comparatively little practised in the present day; certain kinds of paper, however, such as bank-notes, various drawing papers, and printing papers intended for the production of very elaborate editions are made in this way.

Any pattern or name required on the paper is obtained by means of a raised pattern on the wire-cloth mould: consequently, less pulp lodges there, and the paper is proportionally thinner, thus showing the exact counterpart of the pattern. Such devices are known as 'water-marks.' (See also p. 247.)

The Paper Machine.—The paper machine of the present day, with all its ingenious improvements, differs but little in principle from that originally constructed by Fourdrinier. It consists essentially of an endless mould of wire-cloth, on to which the prepared pulp flows, and on which a continuous sheet of paper is formed. The sheet of paper then passes through a series of rollers and over a number of heated cylinders, where it is completely dried.

A modern Fourdrinier paper machine is shown in side elevation and plan in Plates I. and II.

The pulp, after leaving the beaters, passes into a large vessel called the stuff-chest, of which there are one or more to each machine. Two of these chests are shown at C, Plate II. In emptying the beater water is run in to thoroughly rinse out the remaining pulp, the washings also going into the stuff-chests. These may be made either of wood or iron, and should be provided with arms fixed on a vertical shaft, made to revolve by suitable gearing. The arms are for the purpose of keeping the

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PLATE I.

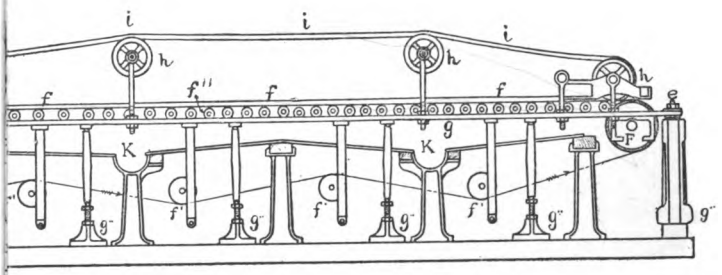

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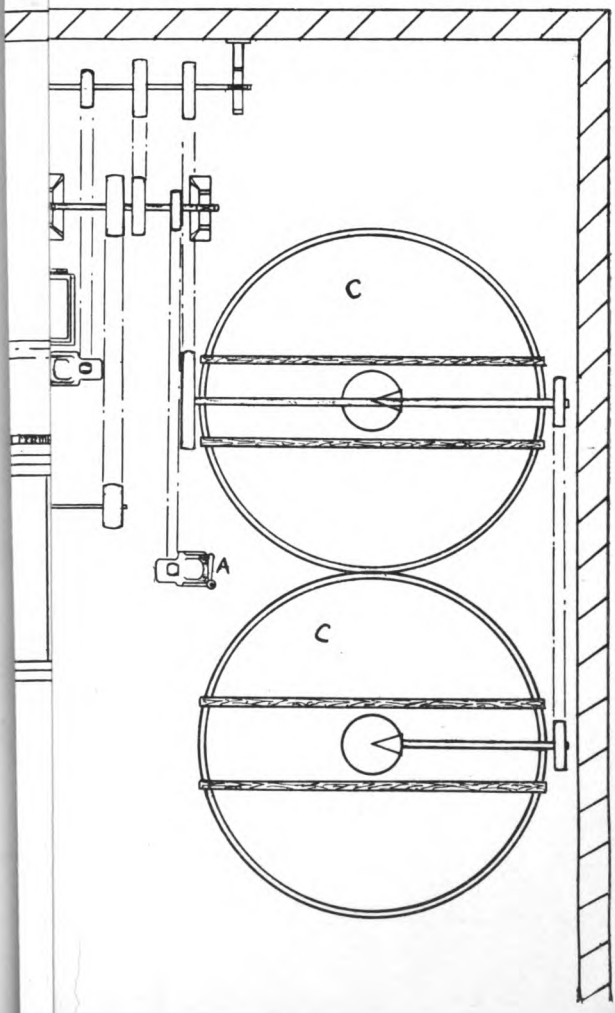
PLATE II.



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pulp thoroughly mixed, and should only work at a moderate speed, otherwise they are liable to cause the fibres to form into small knots or lumps. The pulp is drawn from the stuff-chests by means of the pump A, and is discharged into a regulating-box (not shown). The object of this box is to keep a regular and constant supply of pulp on the machine. It consists of a cylindrical vessel, having two overflow-pipes near the top, and a discharge-pipe near the bottom. The pulp is pumped in through a ball-valve in the bottom, in larger quantity than is actually needed, the excess flowing away back into the stuff-chests, through the two overflow-pipes. By this means the box is always kept full, and therefore the stream of pulp issuing out of the bottom pipe is always under the same pressure. It flows from this pipe, the quantity being regulated by means of a cock, according to the thickness of paper required, directly on to the sand-tables. These may be of various sizes and shapes, but should be so large that the pulp takes some little time to travel over them. They consist of long, shallow troughs, generally of a sinuous form. The bottoms are sometimes covered with woollen felt, or with thin strips of wood placed across the direction of the flow of the pulp, and at a slight angle. These serve to retain any particles, such as sand and dirt, that may have escaped removal in the previous treatment of the pulp, and that are heavy enough to have sunk down during the passage of the pulp along the sand-tables. In some mills, where great care is exercised, the pulp is caused to flow over sand-tables 200 yards in length. The end of the sand-table is shown in Plate II. at S. As the pulp, when it leaves the stuff-chests, does not contain sufficient water for the purpose of making paper, it is mixed, where it enters the sand-tables, with a quantity of water from the 'save-all' (see p. 246), flowing from the box B placed at a higher level.

In some mills, instead of being pumped into the regulating-box, the pulp flows into a small vessel below the stuff-chest, and is lifted on to the sand-table by means of buckets fastened on the circumference of a wheel.

The pulp, after leaving the sand-tables, passes on to the strainers. These consist of strong brass or bronze plates, having

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a large number of very fine V-shaped slits cut in them, the narrowest end being on the outside.

Strainers.—The strainers are for the purpose of removing from the pulp all lumps formed by the intertwining of the fibres, and all pieces of unboiled fibre, which, if allowed to pass on, would show in the paper as inequalities in the surface, or as dark specks. The slits are made narrow at the top, and gradually increasing in width, so as to prevent them from getting choked up. These slits allow only the individual fibres to pass through, and their width varies according to the quality of the paper. They are from 2 to 3 inches long, and they vary in width from ·007 to ·05 inch. They are put at distances of about $\frac{1}{4}$ inch apart.

Several plates, each containing about 500 slits, are bolted together, and form the bottom of a movable box or cradle. The cradle is suspended in a trough and receives a rapid up and down shaking motion or 'jog' to assist the passage of the fibres through the slits.

This is the old form of 'jog-knotter' which is still preferred by many paper-makers, especially for long-fibred rag pulps, in spite of certain disadvantages, such as noise, splashing and liability to overflowing, necessitating frequent attention and removal of the knots. Several improvements of this form of strainer have been patented; in one of the most successful, the 'jog' is imparted to the central axis of the cradle, which is thus kept perfectly horizontal. Many strainers have a stationary cradle, and a suction is produced underneath the plates by imparting a reciprocating motion to an indiarubber or metal diaphragm situated in the trough beneath.

Revolving strainers have come largely into use of recent years. The pulp generally passes through one of these, and then through the ordinary or 'flat' strainers. Two revolving strainers are shown at D D (Plate II.). The Wandel revolving strainer consists of a cylindrical drum perforated with fine slits. The pulp is admitted to the interior of the drum, which receives a rapid vibratory motion in a vertical direction, like that of a 'jog' strainer. At the same time the drum is slowly re-

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volved, whereby clean straining surfaces are presented to the pulp, whilst the knots remaining on the clogged surfaces inside the drum, are carried up to the top, where a strong jet of water, directed from the outside through the drum, washes them into an upper channel, which discharges them through the end of the drum, whence they are conveyed to the auxiliary strainer. Various English firms, amongst which may be mentioned the Watford Engineering Company, now manufacture improved forms of the Wandel strainer. Another type of revolving strainer is that of Reinicke and Jasper, in which the pulp enters a vat surrounding the drum and passes, by a difference in level, assisted by the action of a semi-cylindrical vibrating diaphragm, through the slots into the interior of the drum, whilst the knots which collect on the outer surface are washed off into an external channel by a powerful jet of water directed upwards from the interior of the drum at its highest point.

According to a recent German invention, the drums of revolving strainers are made of hard phosphor bronze wire of a special section wound in the form of a spiral with very narrow spaces between each coil of wire through which the pulp is strained. Although this form of construction is cheaper than the slotted plates, it presents the disadvant ge that the slits cannot be re-closed when worn.

Fig. 47 shows in plan a set of strainers, as manufactured by Messrs. Bertrams, Ltd., similar to those in Plate II., but illustrated somewhat more in detail. This consists of a pair of revolving strainers, A, through which the pulp passes into the shoots placed at the side, and on to the paper machine at E. The pulp which fails to pass through the revolving strainers is washed off on to the flat strainer B, which acts as an auxiliary.

Figs. 48 and 49 illustrate in perspective and cross-section a patent flat strainer manufactured by the same firm under the name of the 'Simplex' strainer, in which the knots flow away automatically to the auxiliary strainer. The 'Simplex' strainer is usually made with a plate-surface of 6 feet or 7 feet by 2 feet 6 inches, the plates being set at a slight gradient across the strainer. The plate trough has an inlet channel along one side

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which distributes the pulp uniformly along the length of the plate, the pulp flowing across the narrow way, thus only travelling about 2 feet 6 inches. At the other side, at the bottom of the slope, is a channel which receives the knots and the pulp which has failed to pass through the slits, and conveys them to the auxiliary strainer. The pulp which has passed through the

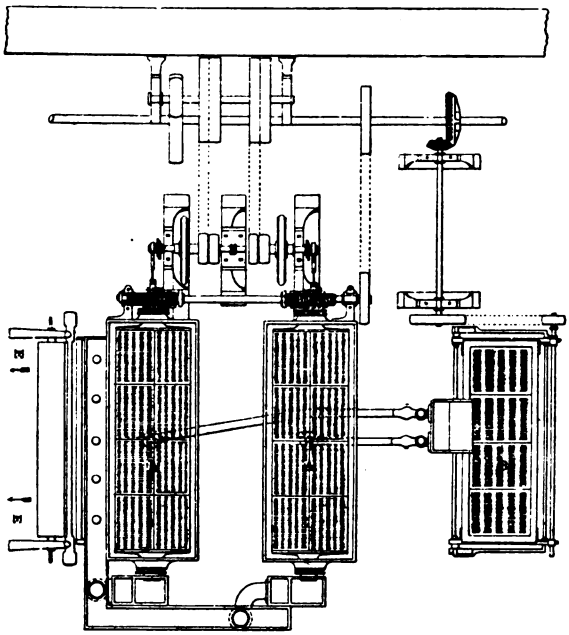

FIG. 47.

plate is collected in the pipe A, and is regulated by the usual box. The vibrating diaphragm E below the plate is the full size of the straining surface, and is operated by the connecting rods driven from the crank-shaft shown underneath the strainer. The amount of pulp allowed to flow away to the auxiliary strainer from the surface of the plate is regulated by a stop-board C, which extends the full length of the strainer, and which is lifted

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momentarily at regular intervals by means of a shaft and cranks worked from a gear-box D.

A different type of strainer, the oscillating drum-strainer, is manufactured by the Watford Engineering Works under the name of the 'Fan' strainer (Fig. 50). This strainer is, to the authors' knowledge, giving excellent results, even with the highest grades of rag-pulps. The slotted cylinder is situated in a trough-shaped vat, and occupies nearly the entire capacity of

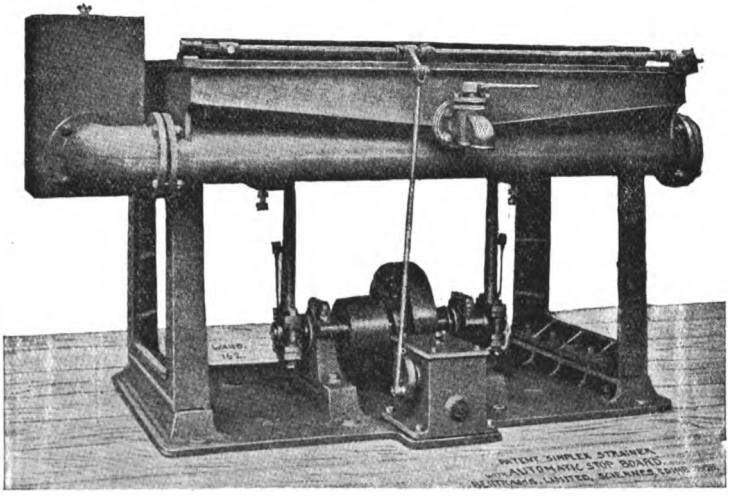

FIG. 48.—SIMPLEX STRAINER.

the trough. The pulp is introduced into the vat and is caused to pass through the slits of the drum under the action of a rapid oscillating rotary motion imparted to the drum by an external shaft. The purified pulp passes away through the hollow journal of the drum-shaft, whilst the metallic particles, knots, and heavy impurities of the pulp are thrown off the surface of the drum by the force of the oscillations, and collect in the bottom of the vat, whence they are removed from time to time with a minimum of waste. It is claimed that in this type of strainer the slits will last without re-closing for a very much longer time than in the flat type.

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After a time, the slits in the plates get too large, owing to the plate having been worn away by the constant friction of the fibres, and as they are very costly, various attempts have been made to invent plans for partially closing them again.

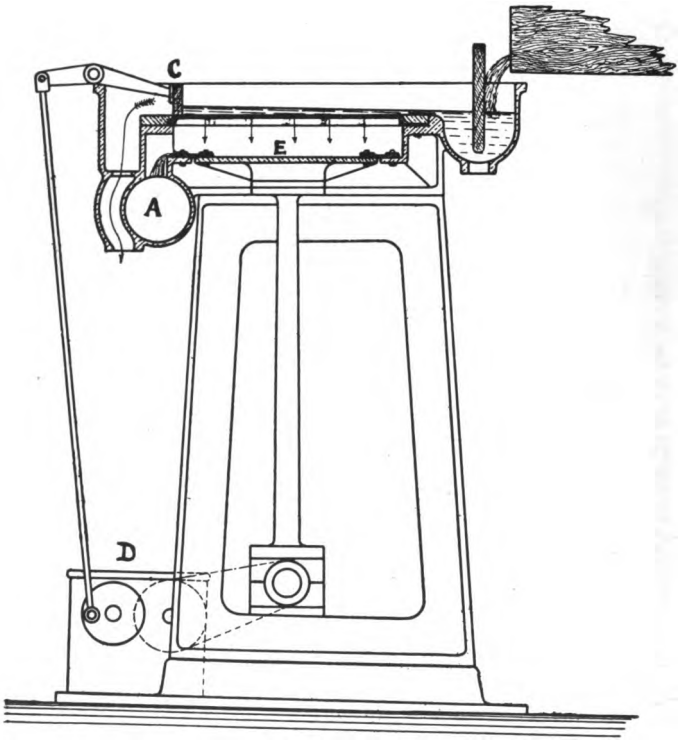

FIG. 49.

Hammering will effect this, but is liable to break the plates. Annandale, of Beltonford, has introduced a method of closing the plates by means of heavy pressure acting on small steel rollers moving on each side of the slit, in which is

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placed a small sheet of metal the exact thickness of the width desired.

Another method of closing the plates consists in filling them up by means of electrically deposited copper or other metal. They can then be re-cut in the usual way.

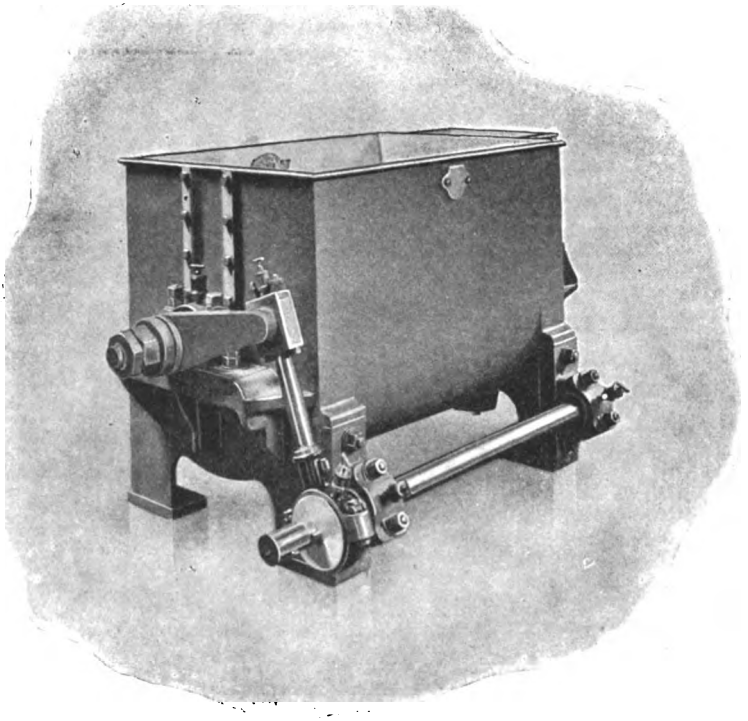

FIG. 50.

In the case of revolving strainers, all that cannot pass through the slits falls to the bottom of the vat, in connection with which it is customary to have an auxiliary strainer, or 'patent knotter,'

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as it is called, shown at E (Plate II.). All fibre that passes through this one, which is of the ordinary flat kind with shaking motion, goes into a box near E', called the 'low box' for 'save-all' water (see p. 246).

The pulp, after passing through the strainers, should be perfectly free from knots and impurities, and in a fit condition for making paper. In the machine shown it passes from the last strainer directly on to the wire, its flow being regulated by a moveable gate, *e* (Plate II.). In some cases, however, it first flows into a small vat, in the centre of which revolves a shaft carrying paddles, with the object of keeping the pulp well mixed. It is carried right on to the wire by means of the apron, a piece of canvas, oil-cloth or sheet rubber, one end of which is fastened to the breast-board *e'* (Plate I.), the other end resting on, and covering the wire to the extent of about 15 inches. The edges of the apron are rolled up to prevent the pulp from overflowing. After leaving the apron, it passes under a gate or 'slicer,' as it is sometimes called, made of two pieces of brass, overlapping each other in the centre, and bolted together. It is made thus to enable it to be lengthened or shortened according to the width of the paper; its height from the wire-cloth can be altered by means of screws, and should be equal at all points, in order to ensure a uniformly thick sheet of paper. The ends of the two pieces forming the slicer are fastened to the frame *f*, or 'deckle' as it is called, and this again is carried by two or more rods stretching right across the wire, and fastened by small upright supports on both sides to the frame *g*. The deckle-frame also carries the grooved pulleys *h*, along which the deckle-straps *i*, endless square bands of indiarubber, move.

The object of the deckle-straps is to regulate the width of the paper; they form, together with the wire-cloth, a kind of mould into which the pulp flows, thus corresponding to the mould used in producing hand-made paper. The width of the paper can be altered by shifting the position of the frame *f*, and also the deckle-straps, which are carried on it, as described, the pulleys *h* being so arranged that they slide along the rods on which they revolve. In order to alter the width of the

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paper it is necessary to stop the flow of pulp on to the wire, and this consumes a considerable amount of time, and often necessitates a partial cleaning up of the machine. Various attempts have, therefore, been made to devise an arrangement whereby the change can be effected while the paper is being made. Several contrivances have lately been introduced, all similar to the one shown in Figs. 51 and 52.

In it the frame *f*, carrying the deckle-strap, is made to slide along the rods *e* by means of the small wheel *b*, and by a similar arrangement on the opposite side, and geared with it. The movable apron *l* (Fig. 51) is wound round the spindle *g*, and is kept taut by the cords *m* connected with the springs *n*. As the deckles approach each other, the excess of apron is wound up;

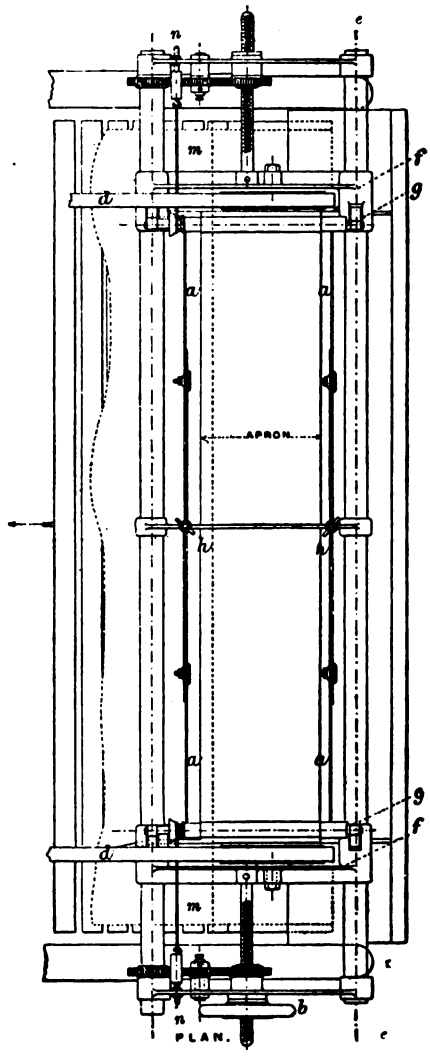

FIG. 51.

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when they are separated it unwinds again. The flow of pulp is regulated by two slices *a a*, which are kept in position by the screws *h*. The whole arrangement is securely bolted to the frame of the machine ; *c* (Fig. 52) represents the breast-roll, and corresponds to F, Plates I. and II.

The thickness of the paper is regulated by altering the supply of pulp to the wire-cloth, and by the speed at which the machine is working. This speed may vary from about 60 feet to as high as 500 feet per minute.

The 'wire' is an endless cloth made of very fine wire, the fineness depending much on the quality of the paper required.

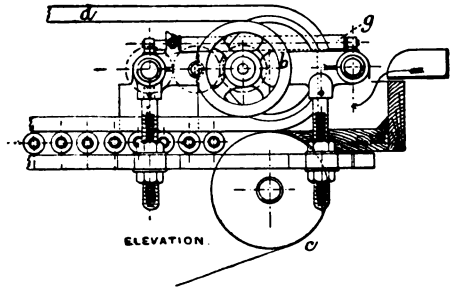

FIG. 52.

The mesh varies from 60 to 70, and even more, strands to the inch. It is not woven endless, but is joined by very careful sewing with wire. Its width varies considerably, some being made as wide as 126 inches ; the length is generally 35–40 feet. It is carried by the breast-roll F (Plates I. and II.), the lower couch-roll G, and the lower guide rolls *f'*, and by a large number of small rolls *f''*.* The latter and the breast-roll are supported by the frame *g*, while the small rolls *f'* are supported by brackets attached to it. The course of the wire is indicated by the arrows. The frame *g* works on two pivots *g'*, and receives a shaking motion from side to side from the rod *j*, in connection with a crank worked by two conical drums H. The supports

* These small rolls are erroneously marked *f* in Plate I.

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g'' are also pivoted at their lower ends to allow for the shaking motion. This shaking motion is given for the purpose of weaving or intertwining the fibres. One or more of the rolls f' can be moved up or down on the support which carries it for the purpose of stretching the wire. There are usually a large number of the small rolls f'', as it has been found by experience that, probably owing to capillary attraction, they cause the water to leave the pulp. Though a large quantity of water thus passes through the wire-cloth it is necessary to assist it by special means. This is done by means of the suction-boxes I, connected by pipes with the vacuum-pumps or with the patent ejectors described below.

This part of the machine, which is called the 'wet-end,' is placed at a slight slope of about 1 inch in its entire length, the lowest end being nearest the strainers. Underneath the wire-cloth is placed a box called the 'save-all' K, connected with the box E'.

In place of a vacuum pump, Messrs. Bertrams, Ltd., who have kindly supplied the drawings of the machine illustrated in Plates I. and II., have introduced the patent water-vacuum ejector arrangement shown in Plate II. Underneath the wire-cloth is placed a box called the 'save-all' K, connected with the low-box E'. The back-water from the paper machine flowing from the 'save-all' K (Plate I.) passes into the low-box E', together with dilute pulp from the auxiliary strainer E (see p. 242). According to Messrs. Bertrams' arrangement, the liquid from the low-box E' is elevated by a centrifugal pump p, into a large settling tank called the 'high-box' B. The ascending main from the pump to the tank B is fitted with an automatic regulating and check-valve operated by a float x, situated in the low-box E'. The pump, being always in motion, draws the water out of the low-box and forces it at a high speed through the ejectors, from which it is again discharged into the low-box. The ejectors communicate by means of pipes y with the vacuum boxes on the paper machine, and the vacuum thus obtained is very efficient and constant. The float x in the low-box E opens or closes the check-valve in the

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ascending main according to whether the level in the box rises or falls. In this way the box E′ can never be pumped empty, and only the excess of water is elevated to the high-box B. The water from the high-box is used for diluting the pulp on the sand-tables, and for washing out the beaters, whilst the sludge and excess of water are filtered in some pulp-saving device about to be described. The water that passes through the wire-cloth contains a considerable quantity of very fine fibres, together with size, alum, clay and colouring materials that have passed through the wire, and which would be lost if some means were not adopted for their recovery. The following

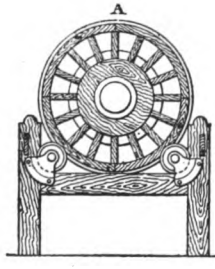

Fig. 53.

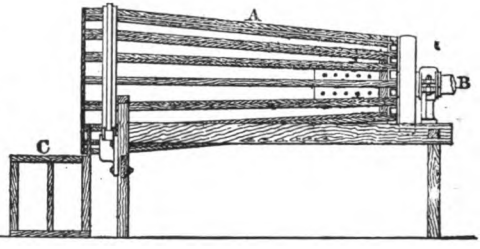

Fig. 54.

numbers will give some idea of the nature and amount of fibres, etc., which pass through. The paper was made from esparto and straw, sized with rosin and starch. It contained 12 p.ct. of clay.

	Grains per Gallon of Waste Water.
Fibre	34·37
Clay	37·10
Starch	1·40

It is almost impossible to utilise the whole of the back-water passing through the wire-cloth for the dilution of the pulp. In some mills the excess of this water is made to pass through a 'pulp-saver,' such as is shown in Figs. 53 and 54. It consists of a conical drum A, the circumference of which is covered with wire-cloth, and it is caused to revolve slowly by suitable gearing. The water enters by the pipe B, and passes through

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the meshes of the wire-cloth, the pulp gradually finding its way to the wider end where it is discharged into the box C. It can then be returned to the beaters.

The pulp-saver can also be used for recovering the fibre from other waste water, such as the wash-water from the washing and beating engines; or it can be used for freeing bleached pulp from water in cases where drainage or hydraulic pressure is not resorted to.

An improved form of pulp-saver has been introduced by E. Füllner, of Warmbrunn, Germany. It has the form of a continuous rotary filter in which the back-water is strained through a travelling felt. A description of this machine will be found in Chapter XV., p. 361.

If any pattern or name is required on the paper it is produced by means of a light skeleton roll, called a 'dandy-roll,' covered with raised wires in the form of the desired pattern, placed between the suction-boxes and pressing lightly on the still moist paper. The paper is thinned where the wire pattern presses, and thus a mark (water-mark) is produced. The other side of the paper has a mark corresponding to the wire-cloth; by using a dandy-roll covered with wire-cloth the two sides can be obtained alike, such paper going by the name of 'wove.'

Paper in which a series of parallel lines are produced is called a 'laid' paper.

Some water-marks are produced by means of a dandy-roll in which the pattern is formed by depressions in the surface. The paper is thus *thicker* where the pattern is formed than in the rest of the sheet. De la Rue (Patent No. 8348, 1884) has patented the use of dandy-rolls so formed as to produce upon the paper the effects both of thickening and thinning.

Imitation water-marks can be produced on the finished paper by subjecting it to pressure in contact with plates on which the design has been produced in relief. In this way very beautiful results can be obtained. (See Patent No. 13,455, 1884.)

It sometimes happens that the wire-cloth slips slightly to

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one side. This can be obviated by the machine-man shifting, by means of screws, one of the rolls provided for the purpose with a movable journal, until its axis is at a slight angle to that of the other rolls. An automatic apparatus has been invented for this purpose. Two brass plates are fixed, one on each side of the wire-cloth, to a long rod, connected by suitable machinery with the screws working the movable journal, so that, as the wire presses against one or the other of these plates, the roll is shifted so as to correct this.

The paper, which, even after passing the suction-boxes, is still very wet, passes with the wire-cloth between the couch-rolls G G′ (Plates I. and II.). These are hollow copper or brass cylinders, the upper one being covered with a tightly-fitting endless jacket of felt. They may also be made of wood (sycamore or mahogany), or of iron, or iron and brass combined. The pressure of the upper couch-roll upon the lower can be regulated by means of screws or levers. They serve to press out water from the paper and to detach the paper from the wire-cloth. By dexterous manipulation on the part of the machine-men, the paper is transferred to the endless felt, travelling over the rolls *k* in the direction of the arrows. It is known as the 'wet felt,' from the condition of the paper at this stage. In its passage along this felt, the paper passes between two iron rolls K, called the first press-rolls, with the object of having the water squeezed or pressed out of it. These rolls are sometimes covered with a thin brass case, and the top one is provided with an arrangement called the 'doctor,' in order to keep it clean and free from pieces of paper that may have stuck to it. The lower press roll is sometimes covered with an indiarubber jacket. The 'doctor' is a kind of a knife placed along the whole length of the roll and pressing against it at every point. The pressure on the rolls can be regulated by means of levers, or, as in the illustration, by the screw *k′*. It will be readily seen that the under side of the paper that has been next to the felt will, in its still moist condition, have taken to some extent an impression from the felt, while the upper side will have been made comparatively smooth by the pressure against the top roll of

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the first press. In order to make both sides of the paper as nearly as possible alike, it is passed through another set of rolls L, called the second press. This time it is reversed, and enters at the back of the rolls; thus the other side of the paper is next the metal, being taken through by the felt (called the 'second press felt') travelling on the small rolls *l*, the paper, after leaving the wet felt, and before being taken on to the second press felt, travels over the rolls *l'*. The second press felt is necessary, because the paper is too tender to withstand, unsupported, the pressure of the rolls.

The paper, after passing the second press rolls, travels over the drying-cylinders M, the number of which varies somewhat. In the machine shown, there are sixteen cylinders. In fast-running machines as many as thirty are employed. Between the second press rolls and the cylinders, a passage allows easy access to the other side of the machine. The paper generally passes alone over the first two, which are only slightly heated; afterwards it is led over the others by means of felts, as shown. The arrangements shown at R are for the purpose of stretching the felts. The cylinders are heated by means of steam, and are generally divided into two sets, between which is a pair of chilled-iron, highly-polished rolls N, called 'smoothers,' the function of which is sufficiently explained by their name. They are also heated by means of steam. The cylinders are usually made of slightly decreasing diameter, in order to allow for the shrinking of the paper on drying. Messrs. G. and W. Bertram introduce into some of their machines one or two small drying cylinders, over which the second press felt travels, the object being to drive off some of the moisture absorbed from the paper. This contrivance is said to give excellent results, and to ensure a considerable saving in felts. The arrangement is shown in Fig. 55. It is especially useful in machines running at a high speed, or in those having limited drying power. After leaving the cylinders, the paper should be quite dry; it is then led through the calenders O, of which there are in some machines as many as three sets, though only two are shown. These are similar to

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the smoothing-rolls, just described. Pressure is applied by the screws O′, or by levers and weights. The friction of the hot calenders on the dry paper develops a large quantity of electricity, which occasionally discharges itself in bright sparks.

It is the practice in some mills to cool and damp the paper before or after passing it through the calenders. This is effected by passing it over a copper cylinder O, through which a stream of cold water runs, and by spraying the paper with water from an atomiser as shown in Plate I.

The degree of smoothness or 'finish' that can be given to the paper by the calenders, depends to a large extent upon the

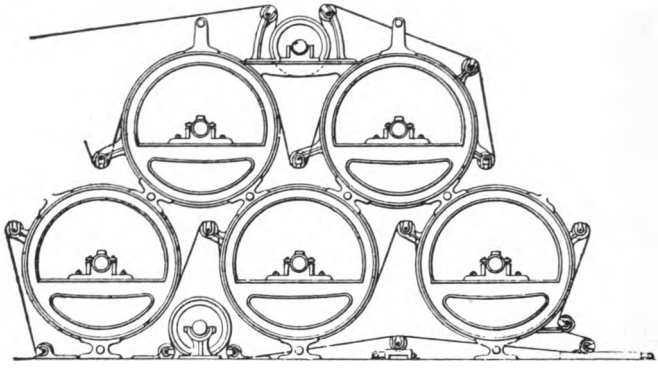

FIG. 55.

degree of moisture which it contains. As it leaves the last cylinder it is perfectly dry, that is to say, it contains only that amount of water which cellulose, from whatever source, always carries. This amount varies slightly with the nature of the cellulose, and with the plant from which it has been isolated, and also with the state of the atmosphere, it being greater on damp days. It would be impossible so to regulate the drying action of the cylinders that the requisite amount of water should always be left in the paper; it is therefore better, in many cases, to dry it as thoroughly as possible, and then to add the water, by artificial means, just before it passes through the

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calenders. This method, moreover, has the advantage of damping only the surface of the paper.

Fig. 56 shows a damping arrangement as manufactured by Messrs. James Bertram and Son. The paper on leaving the last drying-cylinder passes on to two copper cylinders *c*, filled with cold water. Steam passes through the pipe *a*, and issues through a number of fine holes in a pipe running at right angles to the direction in which the paper is travelling, and near to it. The steam condenses on the paper and on the surface of the

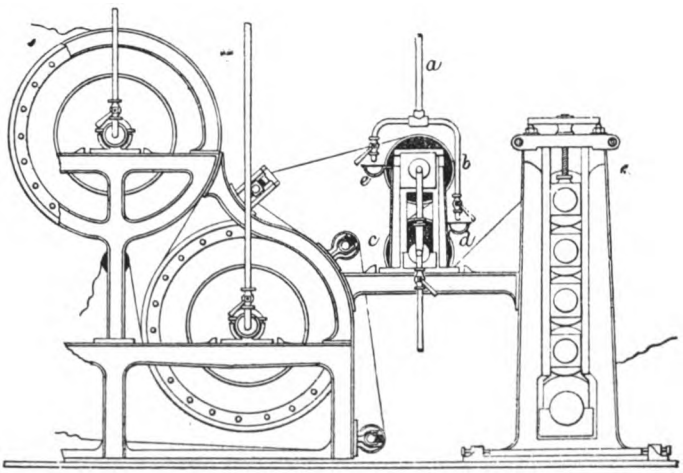

FIG. 56.

cylinders, from which the paper absorbs it. The supply can be regulated by the cocks shown in the drawing. The troughs *d* carry off any excess of condensed water. This form of damping machine is perhaps more generally used nowadays after the calenders for cooling and seasoning the paper before reeling.

Amongst other methods proposed is one by Annandale; it consists in breaking up jets of water into a very fine spray by means of a blast of air.

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The finished paper, after passing through the calenders, is wound on the reels P.

The machine illustrated is fitted with the patent rope-driving gear supplied by Messrs. Bertrams, Ltd. In this arrangement each separate unit of the paper machine is driven by an expanding pulley, the diameter of which can be varied independently of the others. The whole series of pulleys is driven by a single rope, which passes round each in turn, as shown in Plate II. The gearing by which the whole machine is driven is shown in Plate II.

It sometimes happens that, owing to the increased tension due to the contraction of the paper in drying, the paper breaks. It is therefore necessary to alter the speed of some of the cylinders to compensate for this. A rough expedient which is largely adopted, consists in attaching, by means of a mixture of rosin and tallow, a piece of felt to one or other of the pulleys (Plate II.), and thus altering its speed.

In cases where the ordinary 'machine finish' is not sufficiently smooth for the purpose for which the paper is required, the latter is damped and reeled up. When sufficient time has elapsed for the uniform distribution of the moisture, the web of paper is passed through a set of web-glazing or super-calenders (see Chapter X.). For very highly polished surfaces, especially on esparto papers heavily loaded with clay and starch, the 'water finish' may be applied to the paper as it leaves the last drying cylinder M of the paper machine. For this purpose one of the stacks of calenders is fitted with '*water-doctors*,' an illustration of which, as supplied by Messrs. Bertrams, is shown in Fig. 57. The 'water-doctor' consists of a trough A provided with a bronze blade projecting and resting on the calender roll. A pair of these 'doctors' is provided, one for each side of the paper. The trough is partly filled with water, which flows outwards and on to the roll, coming in contact with the underside of the paper as it enters the 'nip.' The supply of hot condensed water is contained in an overhead tank B, and flows down the pipes *b b* into the 'doctor-' troughs on each side of the calender. The 'doctors' have adjustable ends to regulate the supply of water according to the width of the paper. It is im-

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portant that the edges of the paper should not be wetted; this is prevented by blasts of air directed at each end of the 'doctors' against the edges of the paper by means of the pipes *d d*. The lever C tilts the 'doctors' out of position when the paper is being led through the calender, and brings them back again

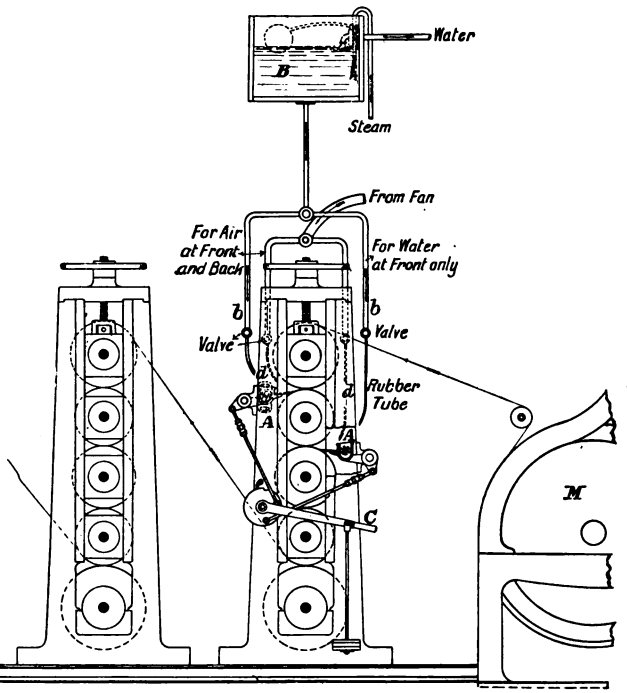

FIG. 57.

when required for use. The calender rolls are heated internally by steam in order to dry the paper after the application of the finish. If desired, colours may be added to the water in the troughs and applied to both sides of the paper.

Tub-sizing.—The foregoing description is of a machine for the manufacture of engine-sized papers; some slight

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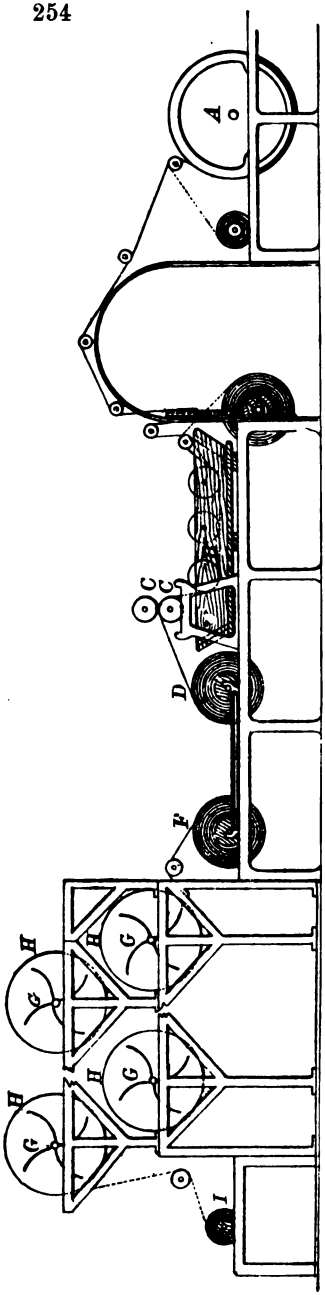

Fig. 58.

modifications are necessary in the case of papers that are tub-sized on the machine. In making the cheaper qualities of tub-sized papers, the paper, after being partially dried over a few cylinders, is passed through a vessel containing a solution of gelatine (see p. 256). It then goes between a pair of rollers, which press out the excess of size, and then again over drying cylinders. The vessel or trough containing the size is filled to overflowing from a tank placed at a higher level; the overflow passes into a lower vessel, from which it is pumped up to the top tank. The size is kept warm by means of a coil through which steam passes, placed in one or other of the vessels containing it. The paper passes between a pair of rollers placed in a trough and dipping into the size. The size may be made to flow through a pipe pierced with a number of holes, the stream running directly on to the web of paper. In the other, and perhaps most general way, at least for the better qualities, the paper is wound off immediately after leaving the last drying-cylinder A (Fig. 58), and sized at some future

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time, or it may be passed directly into the vat B containing the size.

A superior penetration and absorption of the gelatine solution is obtained by a modification recommended by C. Beadle, which consists in increasing the length of the size-trough B and supporting the paper in such a manner that it travels for some distance only on the surface of the liquid before it is immersed by the dipping-roll. By this arrangement the underside of the paper is soaked first, and the air is driven out of the paper from the upper side before the solution penetrates through. After passing between the squeezing-rolls C, it is generally wound off as at D ; and after having stood some time to allow the size to be evenly absorbed by the paper, it is wound off from F, and passed over the cylinders H, of which there may be a very great number, some machines having over 300 of them. These cylinders are made of light spars of wood ; inside them, and revolving rapidly in an opposite direction, are the fans G. The paper in travelling over these drums, is only slowly dried, and is supposed by this means to be more perfectly sized, and increased in strength. It is wound on to reels again at I. Only the first and last two drums are shown. This method was devised to imitate, as far as possible, the sizing process of hand-made paper. Even now, paper that has been made on the machine is sized by hand, after having been cut into sheets, much in the same way as hand-made.

Preparation of Size.—Very pure gelatine can now be obtained in the form of colourless sheets.

Such commercial gelatines are now used in an increasing number of mills with an economical advantage and an improved uniformity in the results. These gelatine sheets merely require soaking for a few hours in the required quantity of cold water, and are then melted by heating the water to about 150° F.

Some mills still adhere to the old practice of preparing their own size.

A great many animal substances, such as clippings of hides, horns, bones, etc., yield gelatine when heated with water. Any of these substances may be used, but wet or dry hides give the

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best results. They are first softened by soaking in cold water for some days: they are then cleansed by washing in a stream of water. The next operation is that of heating with water. This is usually done in iron or copper vessels provided with a false bottom or outer jacket, into which steam may be passed. The hide cuttings are covered with water, and the mass gradually raised to a temperature of about 85° C. (185° F.). In from 10 to 15 hours nearly the whole of the cuttings will have passed into solution as gelatine. This solution is then drawn off and any insoluble substance suspended in it is removed by subsidence or filtration. The hides contain a certain quantity of fat, which collects on the surface of the solution. The residue in the boiler is again heated with water, and the solution added to the bulk. It is of the greatest importance that too high a temperature be avoided, as gelatine is liable, when strongly heated with water, to lose its power of gelatinising.

To the filtered solution of gelatine, which should be, if properly prepared, of a pale colour, a quantity of alum solution is added. The effect of alum upon gelatine is very remarkable. If added slowly it will be found gradually to render it stiff until at a certain point the mass will become almost solid; a further addition renders it fluid again. It is in this state ready to be used for sizing purposes. The amount of alum necessary to produce this effect is 10 to 15 p.ct. of the weight of the gelatine. The alum is also useful in preventing the decomposition of the gelatine, but its chief characteristic is to render the gelatine resistant to ink.

There is no doubt that, besides its action upon the gelatine itself, it has a considerable effect upon cellulose. It is of the greatest importance that the alum or the sulphate of alumina, which can be substituted, should not contain any free acid. This is especially necessary in the case of papers made from rags, in the bleaching of which an acid has been used, one effect of which is to remove all basic substances derived from the boiling or bleaching processes. In the case of esparto and similar fibres, a considerable quantity of such substances are present in the pulp, the result being that the free acid of alum

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is to a large extent neutralised, and its injurious effects prevented.

The effect of the free acid is seen in the weakening of the paper and the destruction of metal surfaces with which it comes in contact. The effect of acid upon cellulose will be found more fully described on p. 14.

Many paper-makers add to the gelatine a certain quantity of soap, the effect of which is to render the paper capable of taking a high finish. The soaps employed should be white and firm, and should be free from rosin. Some soap-makers prepare a

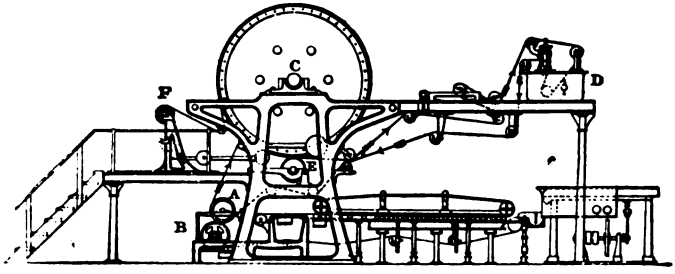

FIG. 59.

special soap for paper-making. They are usually made from tallow, or a mixture of this with a small quantity of cocoanut oil.

If a solution of soap be added to one of alum, a double decomposition immediately occurs, the fatty acid being thrown down in combination with the alumina, and the soda combining with the sulphuric acid. If, however, the soap solution be previously mixed with a solution of gelatine, no precipitation takes place, the mixture forming an emulsion having somewhat the appearance of thin milk.

Various attempts have from time to time been made to size paper in the engine with gelatine, by precipitating it in the pulp after the manner of rosin sizing, but as yet no successful method has been devised.

Single-cylinder Machines.—Modified forms of the original

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Fourdrinier machine have been introduced to meet various requirements. One suitable for the manufacture of very thin paper, or of papers one side only of which is required to be glazed, called a single-cylinder or Yankee machine, is shown in Fig. 59.

It resembles the Fourdrinier machine as far as the couch-rolls A and B. The paper is taken off the wire-cloth on to an endless felt running round the upper couch-roll A and travelling in the direction of the arrows. It is taken from the felt on to the large drying-cylinder C, of about 10 feet diameter, heated

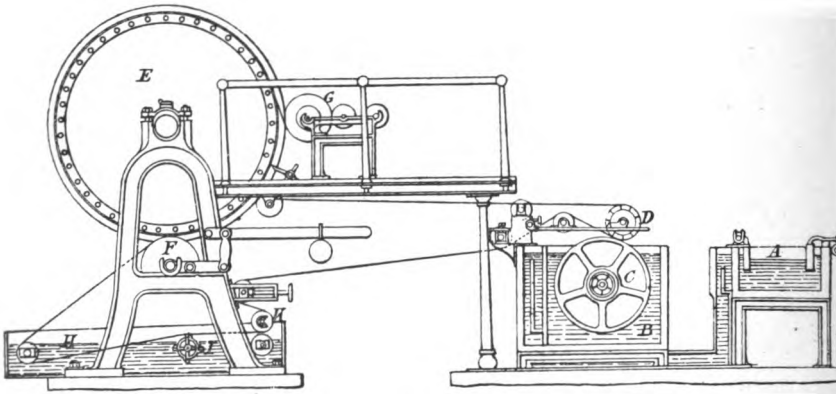

FIG. 60.

with steam. This is carefully turned and polished so as to impart a high gloss to the surface of the paper with which it is in contact. Calender-rolls are sometimes supplied in addition.

The arrangement shown at D is for the purpose of washing the felt. This is necessary to cool and open it out after passing between the cold press-roll E and the hot cylinder.

The paper, after passing over the greater part of the surface of the cylinder, is sufficiently dried, and it is then wound off at F.

A machine of a very different construction from the ordinary form is shown in Fig. 60. The pulp, after passing through the

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strainer A, enters the vat B, in the centre of which a large drum or cylinder C revolves. This cylinder is covered with fine wire-cloth, and on it the paper is made. As it revolves the fibres attach themselves to the wire, and the water passes through the meshes, being assisted by means of a pump. The sheet of paper thus formed is taken on to the endless felt passing round the couch-roll D, and travels along with it to the large drying-cylinder E, heated by steam. It leaves the felt at F, and is then taken on to the cylinder, after travelling round which it is sufficiently dried, and is then wound off as at G. The felt on its return journey passes through the washer H, where it is cleaned and freed from adhering particles by the scraper I. It is squeezed free from excess of water by the rolls K. Paper made on such a machine is weaker than that made in the ordinary way, because it has not been found possible to give a shaking motion to the cylinder, and thus the fibres are only imperfectly felted. Owing to the restricted 'making-surface,' this machine is unable to produce papers of any considerable thickness. But this defect is met by mounting 2–4 making-cylinders in 'tandem' in such a way that the wet webs from the different cylinders are couched in succession as superposed layers on the same felt. A certain advantage of this arrangement is that of being able to vary the composition or colour of the different layers, and thus to control special effects.

A modification of this machine is used for making mill-boards, the difference being that it has no drying-cylinder. The felt carrying the paper passes between a pair of press-rolls, which squeeze out the water. The sheet of paper is then allowed to wind round the top press-roll until of the required thickness. When this happens, it is cut off the roll by a knife. The thick sheets so produced are dried either in the open air or in a room heated for the purpose.

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CHAPTER X.

CALENDERING, CUTTING, ETC.

THE paper, as it leaves the machine, is for many purposes not sufficiently highly glazed, and it is therefore necessary for it to undergo a further process of calendering. This may be done in various ways.

One method, called 'web-glazing' or super-calendering, is to pass the paper previously damped between a number of rolls, alternately of polished iron and very highly compressed paper or cotton.

Since the result of the calendering depends in a very great measure on the proportion and distribution of the moisture in the paper, it is desirable that the damping should be carried out independently of the work on the paper machine, and that the damping machine should be both efficient and capable of accurate adjustment. Such a machine, Milne's Patent Damper,* is illustrated in Fig. 61. The reel of paper shown on the left of the illustration is unwound at a constant tension under the action of an automatic brake. The web is led over two spar-drums, and thence across the machine over guide-rolls to the winding-up reel on the right. In its passage through the machine, the web travels under the damping apparatus, consisting of an endless travelling band of wire-cloth of 40-mesh gauge, shown at the top of the machine. At a point midway between the two end-rolls which guide the wire-cloth, the latter travels in contact with a damping roll covered with a woollen jacket and revolving in a trough of water. The meshes of the wire are thus filled with a film of water, and the cloth then passes on underneath a pipe delivering a blast of air which dis-

* Manufactured by Messrs. Bertrams, Ltd.

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charges the water in the form of fine spray upon the surface of the paper below. The quantity of water imparted to the paper is controlled by varying the speed of travel of the wire-cloth. The spray of water can be varied from a mere mist to a perfect drench, and the jets are extremely regular and fine. The reels of damped paper are allowed to stand for a few hours to permit of the absorption and uniform distribution of the water, and are then ready for treatment in the calender.

The construction of the calender will be understood by reference to Figs. 62 (end elevation) and 63 (front elevation). The reel of paper, as taken from the damping machine is shown

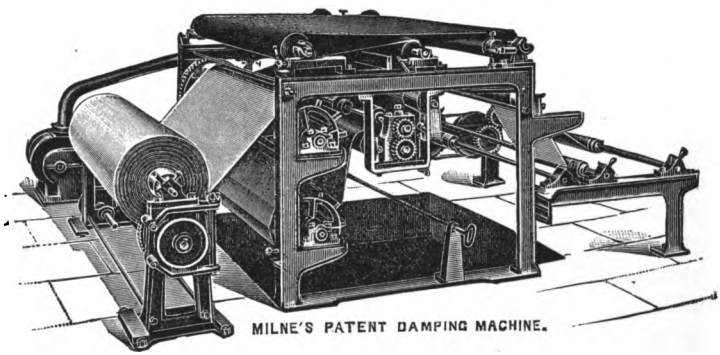

FIG. 61.

at A (Fig. 62) its course over the rolls being indicated by arrows. After passing over the bottom roll, it is wound off on a wooden or hollow iron cylinder B (Fig. 62) driven by the wheel shown by the dotted line C, which is driven by a belt from the wheel E, keyed upon the bottom roll. The whole machinery is driven by the large toothed wheel F (Figs. 62 and 63) which is itself driven by the small wheel G on the main shaft H. The paper rolls are marked P and the chilled-iron rolls I. It will be seen that there are two paper rolls in the middle, for the purpose of, as it were, reversing the paper, and so making both sides alike. Pressure is applied to the rolls by

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means of the screws K, and weights attached at L (Fig. 62) acting on the compound lever M. The brake N, which is applied by means of a screw handle, and clutches the circumference of the wheel O, connected by toothed wheels with the cylinder A on which the paper is wound, is used for the purpose of preventing the paper from leaving the cylinder too rapidly. But for this appliance, the paper would be apt to crease. The paper rolls have an inner core of iron, the paper only extending to a depth of about 5 inches. The iron rolls are hollow, and are connected with steam-pipes, by which they can be heated.

The frames are arranged with simple gearing for separating the rolls when the calender is not in use, thus preventing the marking and burning of the paper rolls. The gear for lifting the reels of paper consists of ropes R with hooks, as shown in Fig. 63.

Another method, known as 'friction-glazing,' employed for giving a very high finish to paper, generally on one side only, is to pass it between a large paper roll and a smaller iron one, the latter revolving at a much greater speed than the former. By this means a very smooth surface can be obtained. It is sometimes assisted by rubbing a small quantity of bees-wax on the small iron roll. The above-mentioned methods apply to the glazing of paper in the web. Paper cut into sheets may also be treated in the same way. Various modifications of these calenders have been devised; they do not, however, involve the application of any special principle.

Plate-glazing, a method that is adapted to hand-made and the better qualities of paper, consists in applying heavy pressure to sheets placed between polished plates of copper or zinc. The metallic plates and the sheets of paper are made into bundles, and the whole is passed between two strong rolls, heavy pressure being communicated to them by means of screws or levers, and weights applied to the ends of the upper roll.

A calender for this purpose is shown in Fig. 64. The bundle of plates and paper is passed along the table *a*; after passing between the rolls *c*, it slides along the table *d*, where it

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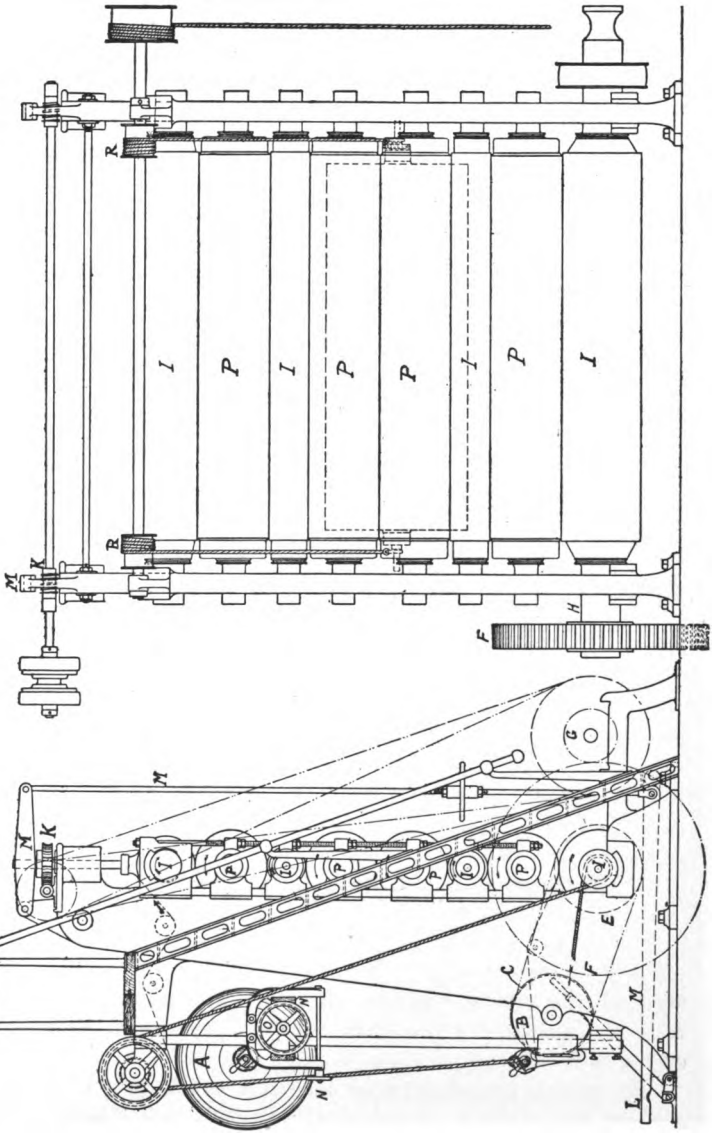

FIG. 63

FIG. 62

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comes in contact with the block *e*; the mechanism is thereby automatically reversed, and the bundle of plates is pushed by the block *e*, through the rolls a second time, and is received

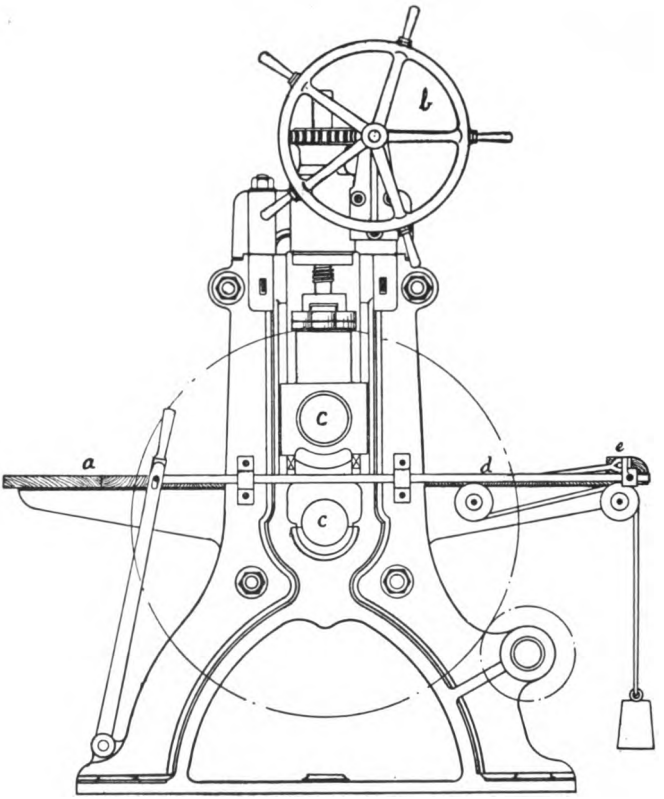

FIG. 64.

again on the table *a*, whence it started. The pressure on the rolls is regulated by the screw-handle *b*, or else by weights on the ends of levers.

By passing paper between rolls on which devices have

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been cut, the 'repped' and other similar papers are produced.

With calender rolls of the ordinary construction, as the pressure is applied at the extreme ends, the roll is liable to assume a slightly curved shape, the effect of which is to produce an uneven surface on the paper, the outer portion of the web being more highly finished than the centre.

This defect is obviated to a very large extent by Schurmann's Patent Anti-Deflection Rolls (Fig. 65). The roll proper consists of an outer shell *a*, through the centre of which, and securely wedged in at *b* is the centre core *c*, the ends of which run in journals, and to which pressure is applied in the usual way. The pressure is communicated to the outer shell at the point of contact *b*, the result being that the parallelism of the

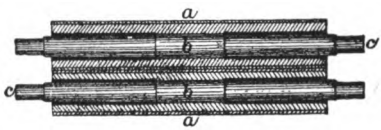

FIG. 65.

surfaces of the rolls is maintained, and in consequence, the paper tends to be equally finished in every direction.

Cutting.—Except for special purposes, such, for example, as for use in a continuous printing machine, paper is usually sent from the mill in the form of sheets. The form of cutter called a revolving cutter, generally used, is shown in Fig. 66. The paper from the webs A is drawn forward by the rolls B; it is then ripped into widths of a convenient size by means of two circular knives, the upper one of which is shown at C. It again passes between a pair of rollers, after leaving which it meets a knife D fastened to the revolving drum E, and pressing against a fixed knife not shown. The cut sheets then fall upon the endless travelling felt F. The action of the knives will be understood by reference to Fig. 67. The edges of the two knives are shown at A and B. The knife B has a

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slot, in which the bolt D slides, and it is kept in position by means of a spring. This spring causes the knife to slide back slightly as it comes against the fixed knife A. The position of the paper is shown by the dotted line C. The knife B is set

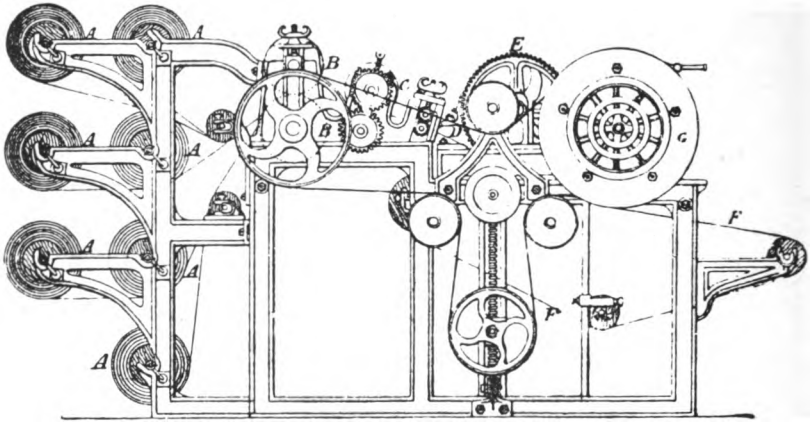

FIG. 66.

on the drum not quite horizontally, so that one end meets the stationary knife a little before the other, thus acting in every respect like a pair of scissors. Fig. 68 shows a pair of ripping-knives. The upper one A is kept in position against the lower

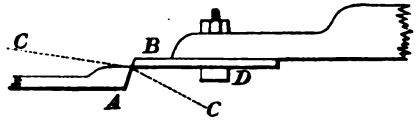

FIG. 67.

one B by means of the spring C. The cutting surfaces are slightly hollowed out, so as to have a sharper edge. The paper is shown by the dotted line D. By altering the relative speed of the drum E and the rolls B, by means of the expanding

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pulley G, sheets of any desired size can be cut. The cutting-knives are sometimes placed inclined to the drawing-in rolls B, so that the sheet, instead of being cut into a rectangle, is cut into a rhomboid. Such paper is used chiefly for the manufacture of envelopes, this shape occasioning a smaller loss when the envelopes are cut out.

Single-sheet Cutter.—It is sometimes necessary, as in the case of paper having a water-mark, that the sheet should be cut with great exactness, so that the device shall come exactly in the centre. The ordinary cutter cannot be relied on for this purpose, and, in its place, a machine called a 'single sheet cutter' is used (Fig. 69). It consists essentially of a large

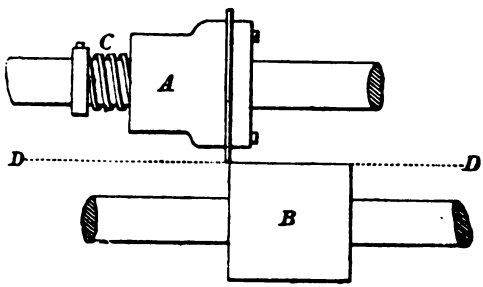

FIG. 68.

wooden drum A, fixed on a horizontal axis, over which the paper is led by a pair of drawing-in rolls B. The paper is held against the drum by a clamp worked by the arm C. The paper is cut by the knife E moving against the stationary knife D. After the cut, the drum describes part of a circle, the paper being still held, so that it cannot go back with the drum. As soon as it has gone far enough, the clamp is removed, and the drum returns, bringing the paper with it. The length of the arc through which the drum moves, and therefore the size of sheet, is regulated by the length of the crank-arm F. If from any cause the cut should not take place at the right time, the man in charge can, by pressing against the clamp,

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retard the motion of the paper, and thus bring back the cut to the right place. The small roller G is for the purpose of keeping the paper always tight.

Guillotine Cutter.—It is sometimes necessary to trim the edges of sheets of paper or to divide them into smaller sheets. This is done by means of a guillotine cutter, an improved form of which, as manufactured by Salmon of Manchester, and called the 'Victory' cutter, is shown in Fig. 70.

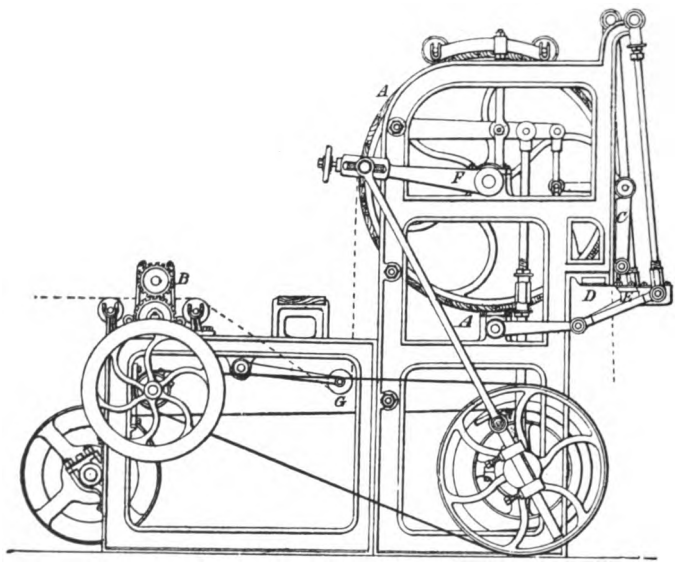

FIG. 69.

The paper to be cut is placed on the table F, touching the back gauge G, which can be brought backwards or forwards by means of the handle H, thus regulating the size of sheet.

The machine is set in motion by means of the lever A, which acts upon a friction-clutch connected with the driving-gear. This causes the knife-bar B and the clamp C to descend. When the latter meets the paper its progress is arrested. The

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knife D, however, continues to descend, and passes through the sheets of paper. By means of slots placed at the back, the knife is made to take a diagonal course. The pressure of the clamp is maintained upon the paper during the cutting operation by means of a powerful spring contained in the tube E.

Finish.—The finish, or surface, given to the paper may vary, according to requirements, from the rough 'cobbly' grain of

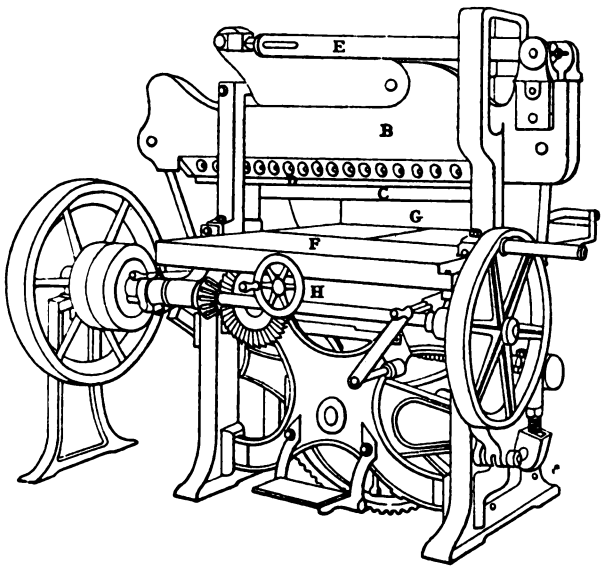

FIG. 70.

certain hand-made papers and machine-made 'antiques,' to the highly polished surface of coated art papers.

The surface of rough-grain papers is an impression of the textile fabric of the felts used for couching the paper. In these cases the paper-maker avoids, as far as possible, the application of pressure to the moist paper except when in contact with felts.

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The mill or machine finish is one which can be varied within wide limits, according to the working of the machine. The term merely indicates that the paper has received its finish on the paper-machine. In hand-made paper the 'mill-finish' is obtained by pressing the sheets of paper one against another, both in the wet state and in the dry state. In this way the felt-marks are removed and the paper acquires a natural grain, produced only by pressure on itself. In machine-made papers the 'machine-finish' can be varied by manipulation of the press-rolls, drying cylinders and machine calenders. A greater or less number of stacks of calenders can be employed, and these can be made to work either cold on nearly dry paper or hot on damped paper.

The next finish in order of smoothness is the 'plate-glazed' finish (see p. 262), rarely applied to any but tub-sized or other papers of sufficient value to bear the cost of the process. Drawing papers with this finish are termed 'hot-pressed,' although in modern practice heat is never employed. In this mode of glazing, the fact that the paper is not damped and the distribution of the pressure of the 'nip' of the calender-roll by the interposition of the metal plates limit the reduction of the 'bulk' of the paper, and confine the action chiefly to the surface of the paper, imparting an impression of high quality which is not obtained by other methods of glazing.

The 'super-calender' finish (see p. 260) is the one most commonly employed for medium-grade writing and printing papers when the 'machine-finish' is not sufficient. The degree of polish obtained under the action of the alternate iron and paper-rolls depends on the quantity of water added to the paper (in some cases up to 30 p.ct.) and on the heat applied to the rolls. In the damp state the paper is quite flexible, and yields to the pressure without 'crushing,' but the reduction in 'bulk' is considerable. The high temperature of the rolls evaporates the added moisture, and brings the sizing constituents into a plastic condition, thereby fixing the fibres in their new positions, an effect which probably has an important bearing on the permanence of the finish.

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The ' water ' finish (see p. 252) is a special finish applied by water-doctors on the calenders of the paper-machine itself. It is cheaper than super-calendering, and its chief use is with esparto papers containing very large proportions of clay for the production of the highly polished surface of ' imitation art ' papers.

The ' friction-glazed ' or burnished surface (see p. 262) is used chiefly for certain kinds of strong wrapping papers, and for certain coated papers.

It stands to reason that the paper nearly always emerges from the drying and calendering operations containing either more or less than the normal quantity of water natural to it in the air-dry condition. In the great majority of cases the finished paper will be drier than the normal, since a moist paper will not retain its finish. On account of the dryness of the paper it is necessary to allow sufficient time of storage for the purpose of ' seasoning,' during which time moisture is absorbed from the air through the edges, and gradually penetrates to the centre. If this process of seasoning be omitted the paper is liable to become wavy at the edges owing to differences in tension set up by unequal absorption of moisture. It is highly desirable that the seasoning should take place gradually whilst the paper is under the pressure either of hydraulic presses or of its own weight. For the latter purpose the dry finished paper is piled in stacks several feet in height with boards inserted here and there to maintain flatness and rigidity. From time to time the stack is pulled down and is rebuilt in the reverse order, so that all the paper may get the benefit of the pressure. This storage under pressure effects a remarkable improvement in surface, flatness and general working qualities, especially in the case of tub-sized papers. In the case of highly glazed papers the re-absorption of water from moist air may cause a certain loss of finish ; this tendency to revert depends partly on the composition of the paper and the specific resilience of the fibres, and partly on want of skill in the manipulation of the calenders. In any case it must be remembered that a glazed surface depends on an artificial state of tension in the constituent fibres, and that this tension is released on damping

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the paper again, so that when the paper is re-dried the finish is almost entirely destroyed.

Sorting.—The sheets of paper are now ready to be examined before being finally sent away from the mill. This is done in the 'Finishing-house,' or 'Salle' as it is sometimes called. This sorting is usually performed by women, who reject the inferior or damaged sheets. These are sold at a reduced price under the name of 'retree.'

Paper is sold in sheets of definite sizes, and is made up into reams containing from 480 to 516 sheets. These sizes correspond to different trade names—such, for example, as crown, demy, royal, imperial, etc. The weight per ream is usually expressed in addition to the name, thus: 14–lb. demy, 18–lb. double crown, etc. In this way the consumer is enabled to make a rough comparison of the thickness of the different kinds of paper.

In making paper it is the duty of the machine-man to examine and weigh from time to time a sheet of the desired size, in order to ensure uniformity. Special lever balances can be obtained, showing at a glance the weight per ream of different numbers of sheets.

The following are some of the sizes of sheets as generally specified for writing and printing papers :—

	Writings.	Printings.
Foolscap	17 × 13½	17 × 13½
Post	18¾ × 15½	—
Demy	—	22½ × 17¾
Royal	—	25 × 20

It is particularly in dealing with such quantities as the above sizes and weights of papers that we become aware of the arbitrary and cumbersome nature of our English weights and measures. It is not for us to argue the question of the superiority of the metric system, but to admit it. Apart from the simplicity of calculations based upon the decimal system of units, there is the more important simplification of ideas in a notation based upon *related* quantities. Thus the ton on the metric system is the weight of the cubic metre of water. The

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English ton on the other hand is related to the yard or unit of length, for all practical purposes, as the dimensions of a ship are to the weight of the crew !

In the weight-measure specification of papers on the metric system the weight per square metre in grammes is a measure from which we pass by an instantaneous process to relative thickness of all papers having the same specific gravity : or by direct measurement of thickness, to the relative gravities of papers which vary in this respect.

The paper-maker in the mill should adopt some uniform standard—preferably the metric system, having reference solely to the physical constants of paper as paper. The arbitrary and conventional weight-sizes of the stationers' trade may be calculated in terms of the systematic standard which should give a direct and simple universal expression to thickness and specific gravity.

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CHAPTER XI.

CAUSTIC SODA, RECOVERED SODA, ETC.

As we have already pointed out, lime and caustic soda are the only alkalis generally employed by the paper-maker for boiling fibrous raw materials; the special cases in which carbonate or sulphide of soda is used have been mentioned in their proper place.

Lime—the oxide of the metal calcium or CaO—is prepared from 'limestones' of varying quality and is also therefore a somewhat variable product. The unavoidable impurities are water, carbonic acid, silicious matters and residues from the coal used in 'burning' the limestone.

The lime should slake readily and the resulting hydrate ($CaO.H_2O$) should form a voluminous impalpable powder.

The preparation of milk of lime requires little or no description, as the operation is a simple and tolerably familiar one. Before using, it should be passed through a fine wire sieve, to keep back sand, coal, and similar impurities which the lime invariably contains.

Caustic soda is prepared by makers who work on the Leblanc system, in various forms, differing from each other in alkaline strength and colour, and of course in price. The lowest quality is what is known as caustic 'bottoms': it consists of that portion remaining at the bottom of the caustic-pot after the clear fused caustic soda has been ladled out, and it contains a considerable quantity of ferric oxide and other insoluble impurities. It is of a dark reddish brown colour, and contains 55–65 p.ct. of alkali (Na_2O), the strength varying with that of the bulk from which it is drawn. When used in paper-making the solution should be allowed to remain at rest,

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in order that the soluble matter may subside, otherwise its use can only be recommended in the preparation of lower grade pulps.

Various grades of caustic were formerly current under such trade terms as 'cream caustic,' '60 p.ct. white'; but the paper-maker in modern times buys caustic of higher grades, of which the following are typical analyses :—

—	78 per cent.	Huson and Hardwick, 77–78 per cent.	76 per cent.	70 per cent.
NaOH	98·11	96·92	95·46	86·60
Na_2CO_3	0·87	1·45	1·99	2·72
NaCl	0·42	0·58	1·55	6·93
Na_2SO_4	0·22	0·73	1·06	3·17
Na_2SiO_3	0·59	0·32	0·02	0·51
Fe_2O_3 and Al_2O_3CaO	traces	traces	0·01	traces
Insoluble	..	..	..	0·21
	100·21	100·00	99·99	100·14

The relative market prices of the various forms of alkali are of significance, and the following are current at this date (1906) f.o.r. makers' works.

PRESENT PRICES F.O.R. MAKERS' WORKS.

	Per ton. £	s.	d.
77 to 78 p.ct. caustic soda, in iron drums	10	10	0
76 p.ct. ditto, ditto	10	7	6
70 p.ct. ditto, ditto	9	17	6
Caustic bottoms	7	0	0
58 p.ct. ash, in bags	4	15	0
Bleaching powder, in casks	4	12	6

All the above-mentioned forms of caustic soda occur in the form of more or less hard masses, and are contained in thin wrought-iron drums, which are filled with the caustic in a fused state.

The best way of breaking open a caustic soda drum is to lay the drum on its side with the seam upwards and then crack the caustic by striking the drum along the seam once or twice for

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its full length with a sledge-hammer. Insert a chisel under the seam and lever it open. The two ends should then fall off and the caustic can easily be separated into pieces by simply inserting the chisel into the cracks and prising them apart.

When the caustic is dissolved in the boiler, its solution should be completed before adding the charge of fibrous raw material.

At the present time there is a considerable industry in concentrated solutions of caustic soda, including those produced directly by the electrolytic process. The following are the degrees of concentration current :—

	NaOH calculated as Na_2O.
90° Tw. containing	32·2
100° „ „	36·2
105° „ „	38·2

The commercial form of carbonate of soda is soda ash. As prepared by the Leblanc process, from the sulphate, it was finished in various forms or grades of purity, to which special trade terms, such as 'caustic ash,' 'refined soda ash,' were given. The Leblanc soda is now, however, displaced by the product of the Solvay process, or 'ammonia' process.

Instead of buying caustic soda direct, it is the custom of some paper-makers to prepare it for themselves from carbonate of soda, which can now be obtained in various forms, some of great purity.

It occurs as caustic ash, containing about 40 p. ct. of alkali as carbonate, and about 10 p.ct. as caustic soda ; soda-ash containing about 52 p.ct. total alkali, nearly all as carbonate ; and refined soda-ash containing 57–58 p.ct. of alkali as carbonate. Some forms of carbonate of soda, such, for example, as those made by the 'ammonia process' (Solvay), are of even greater purity. The method of converting sodium carbonate into caustic soda will be described subsequently.*

Unless the arrangements for washing and draining the lime-

* For a fuller discussion of these questions, see 'The Economy of pure Caustic Soda,' a paper by the Authors in J. Soc. Chem. Ind., 1889.

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mud are very perfect, it is probably cheaper for the paper-maker to buy his caustic direct from the maker. (Infra, p. 290.)

An alternative method of causticising is deserving of mention, as illustrating general principles, though not practically available for the paper-maker. This is the *Ferric Oxide Causticising process*. The principle of this process is the expulsion of the carbonic acid from sodium carbonate by ferric oxide at high temperatures; this oxide playing the part of a weak acid entering into a loose combination with the soda, which is overcome by water in the subsequent lixiviation process, the ferric oxide being regenerated and a solution of caustic soda obtained.

The ferric oxide is therefore continuously available. The main features of the process, disregarding the question of commercial economy, are (1) that it leaves no by-products to be disposed of, (2) that it enables the manufacturer to produce directly, without evaporation, a highly concentrated caustic lye.

Soda Recovery.—In former years, the liquors in which rags, esparto, and other paper material had been boiled, was run into the nearest watercourse; but now, owing partly to the fact that is insisted upon by the Rivers Pollution Act of 1876, and partly because it is remunerative, all these liquors are preserved, and the soda they contain utilised. The method adopted is to evaporate to dryness and ignite the residue. The soda during the process of boiling takes up a large amount of non-cellulose fibre constituents and dissolves them as resinous compounds. These on evaporation and ignition become converted into sodium carbonate. From the previous account of the boiling processes it will be seen that in many cases one-half the organic matter of the original passes into solution in the alkaline lye. The calorific value of this organic matter is considerable, and its combustion therefore under regulated conditions may be made to furnish the greater part of the heat required for concentration of the liquor to the firing point.

The following thermal values indicate the quantitative relationship of typical carbon compounds to heat-energy.

For the series of carbohydrates including the very numerous

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and highly complex anhydride derivatives, the supply of external oxygen for combustion and the thermal effect may be regarded as limited to the carbon. In the process of destructive distillation

The Heat of Combustion of 1 gramme of	Containing C per cent.	In Calories : 1 cal. raises 1 grm. water through 1° C.
Carbon (amorphous)	100	8080 (Thomsen)
Dextrose . .	42	3700
Cane sugar . .	43	3900
Starch . . .	44	4220
Cellulose . .	44	4200

the changes which precede actual flame combustion are complex, and occur both in composition and in the distribution of chemical energy. For a study of these phenomena the student should read papers by Ramsay and Chorley.*

Many raw materials, especially esparto and straw, contain a large amount of silica, a large proportion of which is dissolved by the soda in the form of sodium silicate, in which form also it is found in the recovered soda.

The apparatus for accomplishing the evaporation varies in almost every mill. In some, it is very primitive and crude, consisting perhaps of only a furnace for incinerating the residue, and over it a pan containing the liquor, the latter being heated and evaporated by the heat from the furnace. It is obvious that, with such an arrangement, a large quantity of heat must be wasted. To economise as much as possible of this waste heat, various plans have been devised, the general principle of which is to apply the heat of final combustion of the fully evaporated portion to the work of evaporating *ab initio*. The operations thus constitute a cycle, and the technical problem is that of the most intimate distribution of the heat finally set free and available, so as to produce the highest evaporating and concentrating efficiency.

The following form of apparatus, representing stages in the

* J. Soc. Chem. Ind. See also 'Cellulose.'

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evolution of the most economical systems now in general use, may be briefly described, as they have been extensively employed.

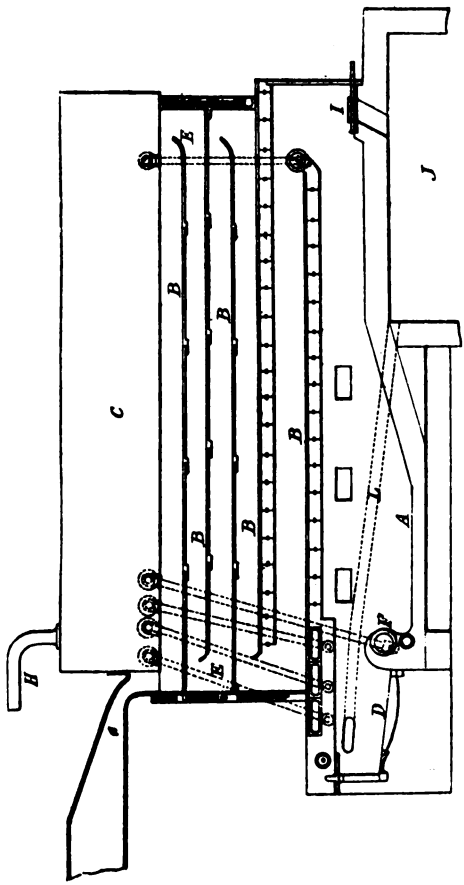

Fig. 71.

The apparatus of Roeckner of Newcastle illustrates the general principles above described. It consists practically of a series of shallow trays, B (Fig. 71), placed in a brick chamber, alternated

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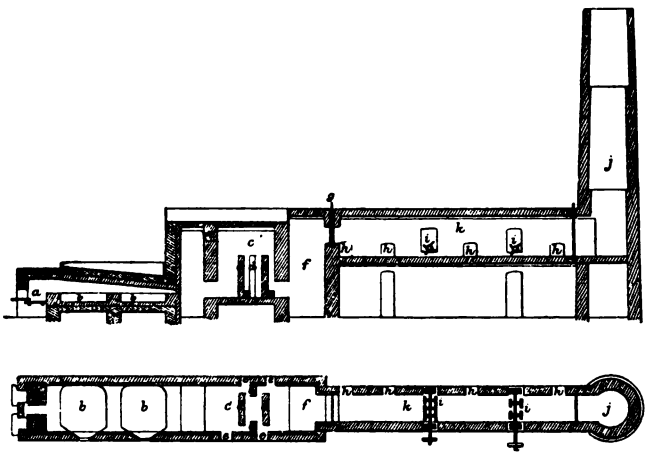
so as to allow the heated air from the furnace below to play upon the surface of each in succession, on its way to the chimney, with which the whole system is in connection. Above the chamber containing these trays, is a large tank C, containing a store of the liquor to be evaporated, placed there so as still further to economise the heat, and from which the liquor runs on to the trays. The furnace A is of the ordinary reverberatory kind; below it, and connected with it by a kind of damper, is a large chamber J, where the calcined residue from the furnace



FIGS. 72 and 73.

is put to cool. thus preventing any nuisance from the smell of the burning mass. The chamber is provided with a pipe L, through which the vapours pass into the furnace. Several pipes E from the furnace pass through the tank, to assist in warming the liquor. The residue, when cold, is drawn through doors from the chamber below the furnace. This residue constitutes the crude ash, or 'recovered' soda.

A very economical form of evaporator is that invented by Porion, a French Distiller, and named after him. It is shown in sectional elevation and plan in Figs. 72 and 73. It is largely

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used on the Continent, and also in England and Scotland. It consists of a large chamber *k*, the floor of which is slightly inclined from the chimney shaft, and through which the waste heat from the furnace *a* passes.

The liquor to be evaporated is run in at the end nearest the chimney from the tank placed above the chamber *c*. A number of cast-iron fanners *i*, dip into the liquor and revolve rapidly, usually at the rate of about 300 revolutions per minute, producing and filling the chamber with a very fine spray, thus presenting a very large evaporating surface.

Between the furnace and the evaporator are placed the chambers *c* and *f*. In *c* a number of brick walls *d* are so placed that the flames from the furnace are intercepted and broken up. The object of this is to give time for all the products of combustion to be thoroughly burnt up, which would not be the case without the 'smell-consumer,' as these chambers are called. This part is an addition to the original evaporator, and was devised by Messrs. Menzies and Davis. The liquor after having been concentrated in the chamber *k* runs into a trough placed alongside the doors *h* and flows into one or other of the furnace beds *b* where it is still further concentrated, and the residue ignited by the flames from the fires *a*. The draught can be regulated by the damper *g*, and also by one placed near the shaft *j*. The doors *e*, in the smell-consuming chamber, are for the purpose of cleaning out. The fanners *i* are worked by a small steam engine, not shown in the drawing. Under properly regulated conditions very excellent results can be obtained with this evaporator. The temperature of the gases near the chimney should not be higher than about 85°. By running the fanners at a very high speed the temperature of the gases may be even further reduced, thus showing the completeness of the evaporation.

This form of evaporator is open to the objection that the whole of the sulphur in the coal employed for the furnaces, finds its way into the recovered soda. It combines with the alkali to form sulphite of soda, part of which is decomposed in the furnace with formation of sodium sulphate, sulphide, and

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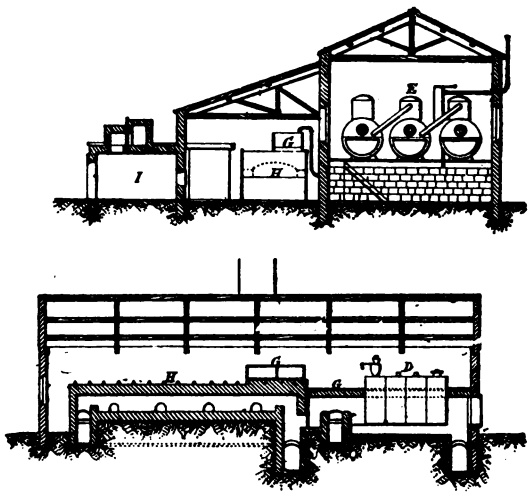
other sulphur compounds. The same objection, of course, applies, though perhaps in a less degree, to all systems of evaporation, in which ordinary flue gases are in contact with the liquor to be evaporated.

The Porion evaporator can be erected at very small cost, and costs but little for maintenance. It is capable of producing $\frac{3}{4}$ ton of recovered soda per ton of coal with liquors of the usual



FIGS. 74 and 75.

strength. It has proved itself to be perhaps the most economical evaporator existing.

An evaporator invented and patented by Mr. Alfred Chapman is shown in Figs. 74, 75, 76, and 77. The evaporation is effected at a low temperature in three vacuum pans E, and with the unusual result that the concentrated liquor gelatinises after leaving the third vacuum-pan, instead of taking the ordinary form of the concentrated products of other evaporators. It is said that this apparatus gives an excellent product, with great economy of labour and water, and with no drainage of foul

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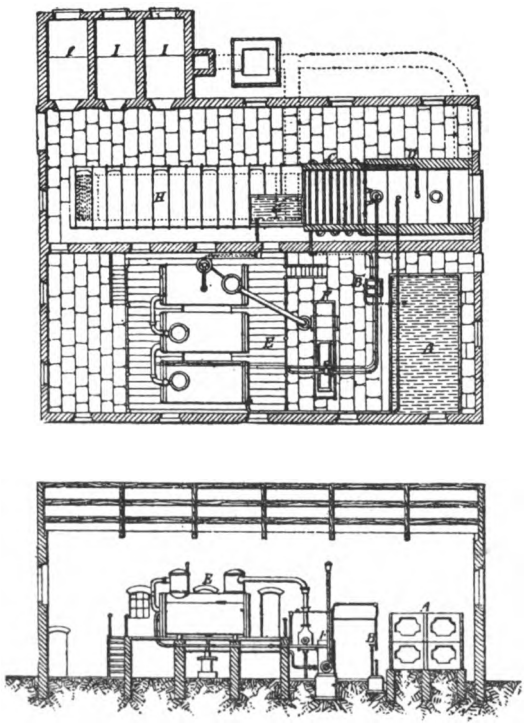
liquor from the buildings. Observations extending over three months have proved that it evaporates 22 lb. of water from the liquor per lb. of coal used under the boiler. It is however very costly to erect.



Figs. 76 and 77.

The waste liquor is discharged into the tank A, whence it is pumped by the donkey-engine B, through the feed-heater C, into the boiler D, which receives heat from the incinerating furnace H, and, in case of need, from an auxiliary furnace shown on the plan, under the feed-liquor-heater. The steam produced

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in D is taken to the first vacuum-pan at E, and having heated its contents, the products of evaporation pass over into the tubes of the second pan; this, in its turn, gives up its products of evaporation to the third, whence they go to the condenser of the vacuum-engine F. Thus the heat from the furnace H is used for incinerating the concentrated liquor on its bed, for heating the feed-liquor in the feed-heater pipes, and for making steam out of the liquor itself in the boiler; this steam finally drives the donkey-pump and vacuum-engine, and causes the evaporation in the three vacuum-pans E. One advantage of this evaporator is the fact that the liquor is evaporated out of contact with the furnace gases.

'*Evaporation by Multiple Effect.*'

In recent years there has been a large development of methods of evaporation based upon the ideal of an exhaustive utilisation of the heat expended upon the liquors to be concentrated. The principle of these methods is that of 'multiple effects,' which may be briefly explained as follows: A liquid is converted into vapour under ordinary conditions of boiling, by overcoming the pressure of the atmosphere upon its surface. The quantity of heat required to vaporise, as also the temperature of the ebullition, will be less as the pressure to be overcome is less. Further, the vapour continuously driven off carries with it a quantity of heat, which is its heat of condition or latent heat. This heat it imparts to any colder body (e.g. a further quantity of the same liquid) with which it comes in contact, direct or indirect; if the quantity of the latter be relatively small, it will raise its temperature approximately to that of the ebullition of the first liquid. If now the pressure (atmospheric) on the surface of the latter be slightly reduced, by any means, it will boil. The vapour from this can be made to boil a third quantity of the liquid, under a further diminished pressure.

The successive effects in economic evaporation consist, therefore, in utilising the latent heat of a vapour given off

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from a liquid under a certain pressure (e.g. that of the atmosphere) to vaporise a further quantity of the liquid under a pressure maintained by mechanical means below that of the first. In certain methods the vapour does its work in the successive effects by passage through systems of tubes, the liquid to be heated being in contact externally ; in the Yaryan system, on the other hand, the arrangement is reversed. The liquid to be evaporated traverses the system of tubes which are heated externally by the vapours. At the end of each effect, the liquid is caused to impinge, in a special chamber, upon a disc : in this way a complete separation of liquid and vapour is effected, each then passing on to the next effect, the former through the tube-system, the latter to the chamber enclosing these. The flow of liquid is maintained by a force-pump, and the diminished pressure by a vacuum-pump suitably disposed. This system differs from that described on p. 278, in that the evaporation is continuous, the dilute liquors entering the apparatus and the highly concentrated liquors leaving it in an unbroken stream. The rate of flow is such that the evaporation of the caustic liquors from wood boiling from 8–10° to 80° Twaddell, in a quadruple effect, requires only a few minutes. At the latter concentration it is ready for the incineration process, which by means of a rotary furnace, is also effected continuously. It is found, moreover, that the excess of heat available from this process is sufficient for the evaporation.*

Whatever be the method of evaporating or concentrating the liquor, the final treatment in the furnaces is much the same in every case. The furnaces shown in Figs. 69 and 70 may be taken to represent the ordinary form. The concentrated liquor is run on to either of the beds *b*, where the last portions of water are driven off by the heat from the fire-places *a*, and the residual mass is ignited until all the organic matter contained in the liquors is carbonised and the soda is converted

* A full account of these methods is given by Griffin and Little, *loc. cit.* pp. 165–170. The student may also consult a treatise by J. Foster on 'Evaporation by the Multiple System,' London : Simpkin, Marshall and Co., 1890.

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into carbonate of soda. This takes place in about 4 hours, according to the degree of concentration of the liquor as it is run into the furnaces. The running in of liquor should be done with great care, as explosions sometimes occur through the sudden liberation of steam on the liquor coming in contact with the hot beds. The charge should be allowed to remain in the furnace until it is thoroughly carbonised and all volatile matters have been driven off, otherwise a nuisance may be caused when the still burning mass is exposed to the air. Roeckner's evaporator is provided with a special chamber into which the charge is drawn (J, Fig. 71).

The composition of the recovered soda varies with the nature of the liquors from which it has been obtained, and, as has been already pointed out, with the form of evaporator employed. It consists essentially of carbonate of soda, together with a certain amount of silicate of soda, if derived from liquors in which straw or esparto have been boiled, chloride of sodium, sulphate of soda, sulphite of soda, sulphide of sodium, and other sulphur compounds, the rest being made up of carbon and insoluble impurities. The amount of soda varies from 35 to 45 p.ct. (Na_2O). The following analysis will give some idea of the composition of recovered soda :—

		Na_2O
*Sodium carbonate	72·33	= 42·306
Sodium hydrate	1·93	= 1·497
Sodium chloride	8·30	
Sodium sulphate	3·95	43·803
Sodium sulphite	0·63	
Silica	7·09	
Carbon	4·70	
Oxide of iron and alumina	·50	
Other constituents (by difference)	·57	
	100·00	

The whole of the soda present as sulphur compounds is not lost, as a large proportion of it is present as sodium sulphite, most of which is converted into caustic soda by the causticising process.

* A certain quantity of potash derived from the mineral constituents of esparto and straw is always present in recovered soda.

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A certain amount of soda is carried forward, partly mechanically and partly volatilised, to the flue leading to the chimney. This accumulates, and may be from time to time removed in the form of fine dust. It contains, besides carbonate of soda, much sulphate and chloride. In two different samples examined by the authors, the amounts of soda (Na_2O) present were 25·0 and 27·1 p.ct.

Causticising.—The next process consists in converting the sodium carbonate in the recovered soda into caustic soda.

This operation is known as 'causticising,' and consists in heating a solution of the soda with lime. The decomposition which takes place is shown in the following equation :—

Sodium Carbonate.		Lime.		Water.		Caustic Soda.		Calcium Carbonate.
Na_2CO_3	+	CaO	+	H_2O	=	$2NaOH$	+	$CaCO_3$

It must be remembered that this is a reversible reaction and that caustic soda will attack calcium carbonate under certain conditions of concentration and temperature, to reform sodium carbonate and lime. Hence the limits of decomposition, which have been determined by G. Lunge as follows :—

P.ct. Na_2CO_3 in Liquor.	Sp. gr. before Causticising.	P.ct. Soda Causticised.
2	1·022	99·4
5	1·052	99·0
10	1·107	97·2
12	1·127	96·8
14	1·150	94·5
16	—	93·7
20	—	90·7

In practice the limit may be taken at 90–92 p.ct. of conversion with a liquor of 1·120 sp. gr.

The ash may be treated for solution in separate vessels. Perhaps the best form of apparatus is a series of lixiviating tanks such as are used for dissolving the alkali in black ash. By this means a nearly perfect exhaustion of the mass can be effected with a minimum of labour. Special tanks are sometimes made for the purpose, provided with mechanical stirrers.

It is essential in dissolving the recovered soda that a high

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temperature should be employed, as otherwise a portion of the soda present as silicate of soda will be lost, as it is only with difficulty soluble, and requires rather prolonged heating with water. Whatever the form of apparatus employed it should be so arranged that, after running off the strong liquor, the insoluble residue may be further treated with water. In the case of the vats mentioned above, this process is made continuous, pure water being run in at one end, and strong liquor flowing from the other. If other forms are used, the liquor after settling, may be run off by means of a pipe passing through the bottom or side of the vessel, and near the bottom, and consisting of two parts, one long and one short. The short part is stationary, and is connected to the longer part by means of a movable knee joint, allowing it to be deflected. The liquor having settled sufficiently, the movable limb is lowered beneath the surface of the liquor which is then allowed to flow through. As the surface of the liquor falls, the pipe is gradually lowered. In this way the clear solution can be run off without disturbing the residue at the bottom. The open end of the pipe is usually covered with coarse wire gauze, to keep back insoluble impurities. With properly calcined recovered soda, the solution should be bright and almost colourless. If at all brown in colour, and if it has an empyreumatic odour, it indicates imperfect calcination. The residue in the dissolving tanks consists chiefly of carbonaceous matter, together with some soda, insoluble matter, etc.

It is interesting to note that the mass of organic matter and alkaline salts, in passing through the several stages of decomposition of the former, contains a series of products which have been little investigated.

The liquor is now ready to be causticised. This should be done in a separate vessel, although it is the practice in many mills to perform this operation in the same vessel in which the solution of the soda has been conducted. A good form of causticiser can be made from an old egg-shaped boiler, by cutting it in two along its length.

It should be provided with two or more vertical steam

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pipes, connected at the bottom of the boiler with a horizontal pipe perforated with numerous holes. The vertical steam pipes should be furnished with injectors, whereby air is drawn in, and forced with the steam through the holes in the horizontal pipe. The stream of air serves the double purpose of thoroughly agitating the liquor and of oxidising any sodium sulphide in the recovered soda. The liquor before causticising should be reduced in strength to about 20–25 degrees Tw., which may be done with the washings of the residue from the recovered soda, or from the washings obtained subsequently from the lime-mud. This strength should never be exceeded, otherwise imperfect conversion into caustic soda is the result. This is due to the fact that concentrated solutions of caustic soda react upon calcium carbonate, forming sodium carbonate, and calcium hydrate, the reaction being the reverse of that indicated in the above equation. If the liquors are very strong in carbonate of soda, and comparatively free from sulphate, they should not be causticised at much over 20° Tw., if they contain much sulphate, and therefore less carbonate, the higher strength can with safety be adopted.

The causticising vessel should be provided with a stout iron cage or basket, into which the lime can be put. This should be securely fastened to the vessel, and should dip into the liquid.

The liquor having been properly diluted, is now heated by means of the steam pipes, and the lime put into its cage. It should be put in in lumps. As the liquor reaches the boiling point, the reaction will proceed rapidly, and the lime will gradually disappear; fresh lumps should be added if necessary. If the liquor is sufficiently heated the causticising will be complete in from two to three hours. The liquor should be tested from time to time; this is usually done by a workman. He withdraws a sample of the liquor, and after allowing the calcium carbonate to subside, pours off a portion of the clear liquid into a glass vessel. He then adds an excess of either sulphuric or hydrochloric acid. If any effervescence takes place, due to the evolution of carbonic acid gas, he knows that the operation of

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causticising is incomplete; the heating must therefore be continued. It is difficult, without an undue expenditure of time and steam, to convert the whole of the soda into caustic; it should however be so perfect, that on testing only a very slight effervescence occurs.

According to Lunge (p. 287) it should be easy to convert as much as 95 p.ct. of the soda, but these results although obtainable in the laboratory, can hardly be achieved on the industrial scale. A conversion equivalent to 90–92 p.ct. causticity in a 24° Tw. liquor is the maximum that is obtained. If paper-makers get 90 p.ct. they have no reason to complain. The actual amount converted can only be ascertained by a careful analysis of the liquor.

The amount of lime used is generally somewhat in excess of the theoretical quantity; 106 parts of sodium carbonate (Na_2CO_3) require 56 parts of lime (CaO): it is necessary, however, to add 60–70 parts. A very good plan is to conduct two or even three causticisings in the same vessel without cleaning out or removing the calcium carbonate, using in the first operation a large excess of lime. The causticising being completed, the calcium carbonate and excess of lime are allowed to settle down, and the clear liquor run off by an arrangement such as that already described in the dissolving process. Fresh solution is then run in and the whole mass heated for some time, until the excess of lime is converted into carbonate. Fresh lime is then added if necessary until the conversion of the carbonate of soda is complete. The liquor is then allowed to settle, and is run off as before: this operation may again be repeated.

The residual calcium carbonate, or 'lime-mud' as it is called in alkali works, is then washed once or twice by running in water, boiling up, allowing to settle, and running off the clear liquor. If these liquors are too weak for use in boiling fibres, they may be used for diluting fresh recovered soda liquor before causticising, or for dissolving the soda.

Some arrangement should be provided for removing as much as possible of the liquor from the lime-mud before throwing it

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away or otherwise disposing of it. This is best done by throwing it on a filter which may be made up of coke and limestone in layers of graduated sizes, and covered at the top with perforated iron plates. The filter is connected with a vacuum pump. In this way very perfect drainage is accomplished, and the mud forms a hard mass on the surface of the filter, from which it can be easily removed with spades. In this form it contains only 50–60 p.ct. of water. If properly washed it should contain in this state only about 2 p.ct. of alkali (Na_2O). By careful manipulation, even this amount can be reduced.

The importance of thoroughly washing the mud can hardly be too much insisted upon. Where proper means are not employed for draining, the washings should be made more perfect. The lime-mud consists chiefly of carbonate of lime, together with silicate, free lime, etc. The following analysis is of a mud obtained by causticising recovered soda derived from the liquors in which esparto and straw had been boiled :—

Calcium carbonate	40·02
Calcium hydrate	5·13
Silica	4·01
Sodium hydrate	2·13
Oxide of iron and alumina	0·30
Water	48·10
Other constituents	0·31
	100·00

As already pointed out the liquors contain a certain amount of soda, as sodium sulphide and other sulphur compounds. The presence of the former, if in large quantities, is objectionable, as it is liable to discolour fibres boiled in liquors containing it. It is therefore best to remove it. This can be conveniently done by blowing air into the liquors during the process of causticising ; this has the effect of oxidising it to sulphate of soda, in which form it is harmless.

The air can of course be blown into the liquor by means of a pump ; the most economical way is to connect with the steam pipe an injector constructed on the principle of the injectors used for feeding boilers and for other purposes. By this means

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a strong current of air is drawn in, and being forced with the steam to the bottom of the liquor, passes through it in a number of fine streams.

If the amount of sulphide present be very high it may be necessary to prolong the oxidising operation beyond the time necessary for complete causticising.

In many paper-mills the causticising is conducted in circular vessels furnished with mechanical agitators. These are more expensive than the simple form described above, and they possess no special advantages. The use of causticisers in which neither mechanical agitation nor agitation by means of air is provided for is exceedingly wasteful of labour, time, steam, and soda. The lime-mud settles at the bottom as a hard mass, very difficult to manipulate.

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CHAPTER XII.

THE QUALITIES OF PAPER REFERRED TO THE STRUCTURAL AND CHEMICAL CHARACTERS OF ITS FIBRES.

Paper in Relation to its Uses. *Uses in relation to quality.*—General knowledge will have made the student aware that the uses of paper fix certain definite lines of demarcation which are the basis of a classification of papers. Thus, we might indicate the following main groups :—

A. Writings and drawings.
B. Blottings and chemical filter papers.
C. Book and other printing papers, including 'News.'
D. Wrappings.
E. A miscellaneous class, which includes papers used for protecting insulations, for certain decorative uses, such as wall papers, cartridge papers.
F. Boards.

It is hardly necessary to point out that these classes overlap in many directions. Thus, papers are at once writings and book papers ; others are suitable both for printing and as finer wrappings. In fact, a classification of papers has only a general significance, and no useful purpose would be served by multiplying details. The broad line of divisions which we have indicated above follow in the main the division of the production amongst the mills. Our purpose is rather to follow up these definite lines so far as they terminate in ultimate chemical and physical properties of the staple raw material. On this subject we may introduce considerations drawn from the historical

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development of the art of paper-making. General knowledge makes us aware that, as far as the qualities of papers are concerned, the art shows very little progress.

The demands of the middle ages in reference to books, drawings and documents, were as exacting as in these days, and the paper-makers were quite equal to their requirements; many in fact maintain, that the papers of the middle ages were superior to any that can be produced at this day.

What we have to recognise as technologists is, that with all the perfection of the art, there have not been any material revelations of new qualities in papers, neither have the essential characteristics in any way changed.

On questions of this kind, we refer the student to special articles, such as Journ. Soc. Arts, March 18, 1898; and Spicer's 'Paper Trade.'

In the middle ages, and indeed up to recent date, the staple raw materials were cotton, flax and hemp fibres in various forms, and it would be a fair inference, therefore, that in these two fibres we find a résumé of qualities, correlative with all the more special effects which are required to be embodied in a finished paper. This inference carries with it, also, the important lesson for the technologist, that processes and products which have been in use for centuries demand special attention from that very fact of their prolonged survival. Survival means fitness in manufactured products quite as much as in the organic world, and we would therefore point out to the student that for a thorough grasp of the working particulars of paper-making, he should make an exhaustive and critical study of the qualities of rag-papers.

In the last century the necessities of civilisation forced the extension of paper-making methods, and the working out of a widely increased range of raw material, and in this country we have seen the successive introduction of esparto, straw, and wood.

It is not to be denied that these raw materials do also introduce new paper-making qualities not to be found in rag fibres, and the reasons will be evident from the discussion which follows.

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We may remark, however, that whereas these fibres, which in the main should be regarded as rag substitutes, are variously used by the paper-makers in different countries, the uses of rag fibres and the methods of treatment are common to all. Of the rag substitutes, we may mention esparto, the use of which is confined to this country. Germany produces papers of a corresponding quality by the use of wood pulp, chiefly of the coniferæ; America, on the other hand, uses a large proportion of pulp from the wood of certain foliage trees.

It will be a useful exercise for the student to acquaint himself with the general lines of production of papers in these leading countries of the world, as a collateral illustration of the division of paper-making raw materials into the two groups, viz. rag fibre, cotton, flax or hemp and rag substitutes, esparto, straw, wood.

Adopting this division for the purposes of the present discussion, we proceed to inquire into the qualities of papers as determined by the physical and chemical qualities of the fibres.

Leaving out of consideration the effect of the sizing agents which are external to the fibrous agglomerate, and passing over such adventitious characters as cleanliness, colour, and chemical purity, we have to deal with the causes underlying strength, elasticity, bulk, opacity, texture, surface etc., in fact the essential characteristics of a finished sheet of paper.

We have premised that paper is an agglomerate of fibrous elements deposited from a liquid medium in which they are freely suspended, and by which they are influenced through bringing into play the colloidal characteristics of the fibre substance.

Strength.—The determining factors of strength are the length of the fibres, the adhesion by mere contact of their surfaces, the number of interlacing contacts between the constituent fibres, and the proportion of gelatinous cementing substances. Strength is evidently not in simple relation to the actual tensile strength of the individual fibres, since paper does not tear merely by the rupture of its fibres, but by the pulling apart of the connecting links binding one fibre with its neighbours. It

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is self-evident that even the strongest fibres, if cut into short fragments in the beater, would give a paper of the weakest kind, therefore 'strong rags' must be suitably beaten to produce a strong paper. The first condition to maintain in the beating is an optimum length of fibre. It is in the process of obtaining this graduated reduction that the tensile strength of the individual fibres is put to the test. This is already apparent in the process of beating to half-stuff, during which the action of the beater-roll is mainly that of longitudinal strain. The resistance of the fibres is still further tried in the whole stuff hollander, where crushing strains are brought to bear in addition to tensile strains. The factor of length of fibre in determining the strength of paper is intimately associated with the secondary factors mentioned above, namely the 'felting.'

The longer the fibre the greater will be the possible number of contacts or linkages with its neighbours. The number of these contacts is still further increased if the ends of the unit fibres be subdivided or frayed out into long fine fibrillæ, since each of these has contacts with other fibres, and the felting of the sheet becomes still more intimate.

Lastly, if the fibre substance has been considerably hydrated or gelatinised, the immediate effect is an increased coherence of each point and surface of contact. This last effect in the case of papers which have subsequently to be 'tub-sized,' may be purposely restricted in order that it may be partially replaced by the addition of an external colloid, which fulfils the same strength-giving functions of the hydrated cellulose, whilst permitting certain other advantages to be obtained.

Elasticity.—Elasticity, so far as it is measured by the elongation under tensile strains, appears to depend on the same factors as the tensile strength. Up to certain limits the elasticity is favourably affected by increased hydration of the pulp, but when the gelatinisation is pushed to an extreme limit at the expense of the length of fibre, as in imitation parchment papers, the tendency is to brittleness. Generally speaking, the greater the tensile strength of a paper the greater is the elongation under the breaking strain, though this rule is influenced to some

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extent by the nature of the fibres. At the same time it is to be noticed, that when, as is nearly always the case, a sheet of paper is stronger in one direction than in another, the direction of the greatest strength is the direction of least elongation, and *vice versâ*. This depends on the relation and disposal of the fibres more in one direction than in the other. This subject has been studied very carefully by C. Beadle and H. P. Stevens,* who showed that the direction of greatest strength in any given sheet of paper corresponds with the direction in which the predominant proportion of fibres is disposed.

Bulk.—It is only in recent years that the idea of 'bulk' has been reduced to systematic numerical measurement (see Chapter XIII., Paper Testing C.B.S. Units). The 'bulk' of a paper is the ratio of the total volume to the actual volume of the solid matters constituting the paper, and is the inverse of the apparent density of the sheet. The quality of 'bulk' is determined first by the composition, fibrous and non-fibrous, of the paper-stock and by the method by which this has been prepared in the beater, and secondly is considerably influenced by the finishing processes, pressing, damping, calendering and glazing.

The inherent 'bulking' tendencies of various fibres in relation to their structure is dealt with in another section of this chapter. It has also been indicated in that section that hydration, or 'wetness' of the pulp, is obtained at the expense of its 'bulking' qualities. A little reflection will suggest the difference between a web of 'free' pulp as it is formed on the wire of the paper machine and a web of 'wet' pulp, viz. in a free pulp the constituent fibres are but little penetrated and swollen by the water, which remains in the interstices between the fibres, and which is then removed by the action of the suction-boxes and press-rolls.

When the water is thus removed and the pressure is released the fibres, owing to their relative resilience, and to the absence of gelatinous cellulose, regain to some extent their original posi-

* Journ. Soc. Chem. Ind., 1905, 775.

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tions. Air is thereby drawn into the interstices previously occupied by water, and a bulky paper is produced. With a 'wet' pulp, on the other hand, water enters to a greater or less extent into the walls of the fibres, swelling up the cellulose to a gelatinous condition, in which it retains its water against the action of suction and pressure, and cementing the fibres together to such an extent that they have not the power to rise again when the pressure is relieved and the paper is dried on the hot cylinders.

The large excess of water thus retained in the web can only be removed by evaporation; the adhesive qualities of the hydrate are maintained during drying, and as it shrinks it draws the fibres with it, compacting the sheet, and giving a paper of high density.

Opacity.—Pure cellulose is inherently a perfectly transparent substance, and when obtained in structureless masses these are found to be translucent. The optical impression of opacity with such a substance is only obtained as a secondary phenomenon depending on the scattering of light from innumerable discontinuous surfaces in the structure of the mass. Multiplicity of reflecting surfaces, therefore, is the cause of the specific opacity of certain fibres, e.g. cotton; discontinuity is the cause of the relative opacity of papers with short fibres as compared with those with long fibres. Moreover, what has been written above with regard to the 'bulking' properties of 'free' pulps and the high density of 'wet' pulps can be applied with equal force to account for the opacity of the former and for the transparency of the latter. The air spaces between the fibres of the paper, which determine the quality of 'bulk,' also involve the multiplicity of discontinuous reflecting surfaces, whilst the structural continuity of a dense hydrated paper equally involves its transparency. The great increase in transparency which takes place after the tub-sizing of a water-leaf paper is also referable to the same cause. On the other hand, a divergence of the two qualities of 'bulk' and opacity is to be noted with regard to the influence of mineral loading materials, especially those of a specifically opaque nature. Whereas the interposition of

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heavy minerals in the place of air between the fibres decreases the 'bulking' qualities of the paper by increasing its density, it materially increases its opacity by substituting a definitely opaque surface for one which is only apparently opaque by partial reflection.

Texture and Surface.—These qualities may be dealt with here in so far as they depend on the preparation of the stuff, and not on the manipulation of the machine or the degree of calendering. The texture or 'look-through' of the paper and the plainness of the watermark are desirable qualities, which, like the qualities of bulk and opacity, are arrived at as the result of a compromise with regard to the quality of strength.

Even when the refining and mixing of the stuff and the manipulation of the paper machine have been performed with the greatest possible care, papers which are distinguished by a maximum mechanical strength (depending as this does on great length of fibre and 'wetness' of the pulp) are for this very reason defective so far as the quality of the 'look-through' is concerned.

A long 'wet' pulp possesses a certain degree of immobility on the machine wire, whereas the elements of a short-fibred 'free' pulp are at liberty to take up a more uniform distribution so long as there is sufficient water to float them. The friction presented by contact with the machine wire of the bottom-most layers of the stuff is communicated, in the case of long fibres, to the upper layers and causes a partial clotting, which imparts a 'wildness' to the finished sheet. 'Wildness' in texture involves an unevenness of surface, which is only partially corrected by the pressure of the couch, press and glazing-rolls. In the case of shorter fibred pulps, the fibres are deposited in uniform layers, the longer fibres gravitating to the bottom, whilst the shorter ones, remaining longer in suspension, fill up any inequalities which may have occurred, thus improving both the texture and the surface. It may be remarked that the English maker of strong high-class papers has, owing to the prevalence of tub-sizing in this country, a considerable advantage over his Continental competitors, which makes the description 'English paper' synonymous all over the Continent with excellence of

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strength and quality. Engine-sized papers depend for their strength entirely on the preparation of the fibres with the consequent disadvantage, in the case of the strongest varieties, of inferior texture and other qualities. The manufacturer of tub-sized papers, on the other hand, is able to make a relatively much weaker water-leaf with shorter 'freer' stuff, thereby obtaining an excellent texture and surface, and is then in a position to double its strength, if he so desires, by the process of tub-sizing with gelatin.

Damping Stretch.—For certain special printing papers, mainly for illustrations, it is necessary that the paper should show a minimum alteration in the dimensions of the sheet when the latter is damped. This quality of minimum expansion on damping is obtained by the preparation of a short-fibred 'free' pulp, such as is yielded by cotton rags or esparto cellulose, and by careful manipulation of the tensions during manufacture.

Here again the function of 'bulk' in relation to air spaces between the fibres is brought into play as the determinant factor.

As the fibres of the paper swell up with the absorption of water, their expansion takes place to a great extent into the surrounding air-spaces; moreover, the relative shortness of the fibres enables them to change their dimensions with the least possible disturbance of the position of their neighbours. In a very 'wet'-beaten pulp, in which the position of the fibres relatively to each other in the sheet of paper is absolutely fixed by the adhesive action of the gelatinised cellulose, and in which the quantity of water re-absorbed by the cell-substance is considerably greater, the change in the dimensions of the constituent elements is accompanied by a corresponding change in the dimensions of the whole sheet.

This effect is noticed in an exaggerated degree in the case of 'grease-proof' parchment papers, in which the changes of dimensions are observable even with changes of weather.

Beadle and Stevens * have shown that the expansion of paper on damping takes place in different degrees in the

* Loc. cit.

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different directions of the sheet, and that the direction of minimum expansion coincides with the direction of maximum strength, which is also the direction in which the longitudinal disposal of the fibres predominates. This observation is quite in accordance with measurements made by von Höhnel,* who found that vegetable fibres, when wetted with water, expand 20 to 30 p.ct. in diameter, whereas the expansion in length amounts to barely 0·1 p.ct.

The paper-maker, in selecting and treating his raw materials, has in view a particular combination of these properties, characteristic of the particular fibres, as well as such a range of variations as may be determined by his processes. So far as typical characteristics are concerned we now proceed to discuss the leading or staple paper-making fibres.

Cotton.—The external characteristics of cotton, as observed in the mass, is expressed by its conventional description as 'cotton wool.'

Cotton fabrics, whether yarn or cloth, are distinguished by opacity and lack of lustre. The minute structure of the ultimate fibre has already been dealt with on p. 98.

It represents a flattened, twisted ribbon, this twisting being probably caused by internal strains during the process of growth and ripening. The cell wall is seen to be made up of minute strands or fibrillæ, giving the appearance of a tube of reticulated fabric. It will be evident that in reducing the cotton fibre to paper-making length it undergoes a series of fractures, but the fracture of a reticulated fabric is somewhat short, and the splitting cannot prolong itself to any great extent along the axis of the fibre.

The mature fibre is characterised by the presence of a cuticular envelope, which is differentiated from the inner cell-substance. It shows itself more resistant to chemical actions, including that of water. This cuticle is, however, broken and to some extent removed by the bleaching and boiling operations to which cotton textiles are subjected, and the paper-maker in

* 'Die Mikroskopie der technisch verwendeten Faserstoffe,' 2nd ed., p. 20.

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handling cotton rags will find that they will vary under treatment according to their previous history.

From the earlier section of the work, it would appear that cotton, of all the raw plant fibres, is the nearest to pure cellulose, and the removal of the non-cellulose impurities requires the least amount of chemical attack. One consequence of this is that the fibre substance shows a maximum resistance to disintegration by the chemical actions to which all organic bodies are exposed, that is, under conditions of natural wear and tear cotton will show the least amount of degradation. This resistance takes effect also in relation to the penetration or saturation of this substance by water in the mechanical action of the beater, or when this action is fortified by chemical agents.

Thus, the general résumé of the paper-makers' experience in working cotton pulps is that they give soft, absorbent, and bulky papers; but with increasing age, wear and tear, or equivalent chemical and mechanical actions upon the original raw material, there is a progressive modification of these typical characteristics in the direction of those of the linen or flax fibres which we now describe.

Flax-Linen.—The ultimate fibre has been described on p. 99, and the chemistry of the raw flax has been dealt with on p. 71. The ultimate fibre shows a length of 20 to 60 mm. with an average of 35 mm. The general form is polygonal, with a smooth contour and small central canal. Owing to the parallelism of the fibres in the bundle or filament, which they retain in working, flax yarns are relatively lustrous, and this lustre is very much increased in the process of beetling or hammering to which flax goods are subjected. In relation to water and hydrolytic agents the cellulose is more sensitive than cotton. The solid structure of the flax fibre enables it to withstand a large amount of pressure under the beater-roll. The minute structure of the cell wall is indicated by striations which mark the disposition of fibrillæ developed parallel to the axis of the fibre. From this it follows, that the fibre-cells under pressure and beating tend to split longitudinally or axially, and the torn ends of the fragments are marked by tufts of these fibrillæ.

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These tend to interlace in the paper-making process at numerous points and in various planes, and have an important function therefore in binding the sheet together, conferring its special tensile qualities.

In beating for fine papers, such as cigarette tissues, and banknotes, the pressure on the beater-roll is regulated to carry this longitudinal splitting of the fibre-cells to an extreme limit.

These structural qualities are associated with a much increased hydration capacity, which is also taken advantage of in the beating. The long beating has the effect of surrounding the flax-fibre with a gelatinised envelope of the hydrate, which causes it to hold water, and to part with it very slowly on the paper machine.

Under the action of the press-rolls the adhesion of the gelatinous elements cements the fibres together and produces in the papers the characteristic toughness and 'rattle' which differentiate linen papers from those made from cotton.

Hemp.—Hemp fibres, both the filament and the ultimate fibre, show a close resemblance to the flax. The filament, however, does not divide under the heckling and other preparing treatments, with the same facility, and this material is not spun or woven to such fine fabrics as in the case of flax. On external characteristics, except that of colour, it is impossible to distinguish hemp from flax canvas, and this difficulty, which exists in the sorting-room, is also encountered microscopically in the analysis of the papers. The two fibres when thoroughly beaten are, in fact, practically identical, and this is also true of their paper-making quality. It may be noted that the section of hemp fibre, p. 100, shows a central canal more developed than in the case of flax, and the cell walls are correspondingly thinner. Chemically there is a slight differentiation, as the raw hemp fibre possesses a zone of lignification, and the cellulose when isolated shows in consequence a tendency to somewhat less resistance to chemical action: as from the thinner wall it is also less resistant to the mechanical action of the beater-roll.

Rhea, Ramie.—This fibre has been very little employed in this country. It is stated to be the main constituent of

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certain banknote papers in Continental countries. It has obviously paper-making qualities of a high order, and would generally resemble cotton in working.

With the general increase in the textile use of rhea which is now to be noticed, it is probable that paper-makers in this country will have opportunities of acquiring ramie wastes of various kinds including 'rags,' and they would therefore do well to acquaint themselves with the paper-making qualities of the fibre.

We have now dealt with the paper-making qualities of the leading fibres of the 'rag' class in reference to the ultimate structural features of the fibres themselves, and the general chemistry of the fibre substance, and have shown that these cover a wide range of variations, corresponding with a similar range of effects embodied in the finished papers. We need only cite the soft and absorbent cotton blottings by contrast with the hardest linen 'banks' and 'loans' to show what a very wide range of effect is covered by this group of raw materials.

It is evident that by blends and combinations the intermediate effects or qualities are obtained at will.

In addition to the primary causes, there are a number of secondary qualities which have to be taken into account in dealing with these fibres in their manufactured forms. These result from the various modifying influences which are associated with (1) spinning or twisting of the yarn; (2) density or closeness of woven fabrics; and then again (3) the amount of wear and tear, chemical and mechanical, which the fabric may have undergone before it reached the paper-maker.

These differences are taken into account in the sorting of the rags, and the characters of these sorted rags are taken into account in the composition of the paper-maker's furnish.

A few general particulars will indicate the basis of this classification or sorting and selection for particular effects.

Rags.—New cottons, in the form of knitted or loosely woven fabrics, are selected for maximum length of fibre and minimum hydration in beating. They, obviously, represent the nearest

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approximation to the original fibre. Such material can be used for filter papers, for the reason that the required paper-making length is quickly got in beating, together with free-running stuff and bulk in the finished paper.

Old cottons of the same class (muslins) are preferred, for similar reasons, for short-fibred blotting papers.

New cottons, in the form of shirtings or calicoes, represent relatively hard-spun yarn and closeness of cloth; they would require, therefore, a much more severe beating treatment, and in the time necessary for reduction in the beater to units of good average length, hydration goes much further with corresponding 'wetness' in the stuff.

New coloured rags which require a drastic chemical treatment for bleaching to a white cellulose, are already somewhat degraded chemically, and have an increased tendency to hydration and wetness of stuff. Old rags are of course still more degraded both by mechanical wear and tear, atmospheric influences, and laundrying, thus show still less resistance in the beater, and work through much shorter and relatively 'wetter,' compared with the time they are in the beater. The selection of linen rags is guided by somewhat similar principles, new linens being chosen for pulps of maximum length and 'wetness,' e.g. for strong, thin papers, whilst old linens are generally employed for imparting some of the specific characters of this fibre to papers composed largely of cotton.

We now have to consider three groups of fibres which, in their paper-making qualities, may be treated here as rag substitutes.

These fibres are the various types of wood celluloses, esparto cellulose, and straw cellulose. Speaking roughly, apart from any special treatment in the beater, the cotton substitutes are soda wood pulp, poplar wood pulp and esparto, whilst the linen substitutes are sulphite wood pulp and straw.

Wood Celluloses.—The wood celluloses are divided, naturally, into those obtained from foliage trees, of which poplar may be taken as the type, and those obtained from various species of coniferous woods, which represent by far the

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largest proportion of the total manufactured. In structure and working quality foliage wood celluloses approximate rather to the class of straw celluloses, occupying a position between that of esparto and straw, although chemically they belong to a different group. The coniferous wood celluloses are classed according to the method of their preparation, as sulphite pulps, and soda pulps (including sulphate pulps), and each sort is divided into 'strong' or low-boiled, and 'easy bleaching' or high-boiled types. There is of course no definite line of division between these types, one merging into the other as the severity of the chemical treatment is increased. The processes employed for the isolation of the cellulose depending on processes of hydrolysis, either acid or alkaline, assisted by specific affinities between the reagents and the soluble products, it follows that the cellulose, being itself also susceptible to hydrolysis, must be progressively modified and weakened in proportion as the severity and duration of the treatment necessary for the elimination of the non-cellulose are increased. Thus in the preparation of a highly boiled pulp, any treatment in excess of the minimum necessary for the decomposition of the lignocellulose complex proceeds at the expense of the yield and quality of the cellulose. Since with such a variable raw material as wood, it is almost impossible to predict the precise amount of boiling required to produce a given degree of resolution, and since the boiling therefore depends on personal judgment, it is not a matter for surprise that variations, whether in the direction of under-boiling or in that of over-boiling should occasionally arise.

Structurally the constituent fibres of coniferous wood pulps may be roughly divided into two types derived respectively from the summer growth and the autumn growth. The former are relatively very broad and flat, with very thin walls on which the pitted pores are easily discernible, whilst the latter possess a more truly fibrous form, rounder and narrower in section with thicker walls very similar to the jute fibre, and in some cases with a strongly pronounced reticulated structure resembling that described above for the cotton fibre ; both types of cell are of

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good length. Generally the broad flat type of cell predominates, and may be taken as the determinant factor in the character of wood pulp papers. Their breadth and flatness cause them, when reduced in length by the beating operation, to lie very closely one over another, so that the paper is lacking in air-spaces or bulk. The thinness of the cell walls, and the consequent ease with which reduction and hydration take place in the beater, give the paper a translucent and relatively hard and brittle character which is described by the paper-maker as 'woody.' As a result, for bleached papers in which characters other than merely strength are required, coniferous wood cellulose, prepared by the sulphite process, is only rarely used by itself in this country. It is generally blended, in proportions which may vary from 10 to 75 p.ct. with some fibre more rounded in section, more opaque, and more flexible, which will counteract the defects of the wood. In this country, esparto for cheap papers, and rag fibres for the better sorts are generally chosen for blending with wood pulp. In America, poplar wood pulp, and on the Continent, straw pulp are used in place of the esparto. Wood celluloses prepared by the alkaline processes (soda and sulphate pulps) generally possess the above defects to a less pronounced extent than those boiled by the acid sulphite process, since the alkaline treatment appears to leave the fibres in a softer and more curly condition than the acid treatment; blends of soda wood pulp and sulphite wood pulp are therefore fairly common. Of the group of cellulose fibres now under discussion, only those of the coniferous woods are long enough to require any actual reduction in length in the beaters; the pulps from foliage woods, esparto, and straw consist in the main of fibres of convenient paper-making length, and the operation of beating is confined to brushing them out, separating the bundles and mixing the constituents of the paper. Except for wrapping and strong envelope papers, however, the fibres of the coniferous wood pulps generally have to be reduced in length; this reduction cannot take place as in the case of the rag fibres with the simultaneous teasing out of the cut ends and the production of more or less long and flexible fibrillæ. The broad, flat type of cell has no apparent structure in its wall,

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and tears off sharply under the action of the roll, whilst the reticulated structure of the more fibrous type of cell is so pronounced that the points of fracture are only splintered. The production of loose-ended fibrillæ would therefore be reduced to a minimum, even if the fibres were mechanically capable of withstanding the drawing tension required to free the fibrillæ. For this reason beaten wood pulp is deficient in felting properties, and the binding of the sheet of paper must be assisted by the admixture of some finer fibres, such as esparto.

The hydration capacity of the wood celluloses is very great. When it is remembered that 50 to 60 p.ct. of the substance of the wood is dissolved away in the process of manufacture and that, owing to the fully lignified nature of the raw material, the greater portion of this loss is borne by the actual cell walls of the fibre elements themselves, it will be understood that the cellulose residues of the fibres must have a certain porosity, and represent, chemically, a more sensitive condition than the normal cotton cellulose. Such a condition favours combination with water during the beating, and the production of gelatinous hydrates, which is one of the causes of the transparency and harshness of a wood pulp paper. Nevertheless, this high hydration capacity of wood pulp, if judiciously applied, may be turned to very valuable uses. Mixed in small proportions with cotton pulp or esparto pulp, it can be made to fulfil many of the functions of linen, imparting stiffness, 'rattle,' and even strength by supplying the colloidal cementing substances in which these pulps, as ordinarily prepared, are deficient. Furthermore, chiefly on account of their long fibres and ready hydration, wood pulps, especially those of the unbleached, low-boiled type, when used alone, are capable of giving wrapping, cartridge and imitation Manila envelope papers of very great tensile strength and resistance to tearing. As an extreme example of the hydration of the wood pulps, the very characteristic grease-proof, imitation parchment papers may be cited. These papers are practically transparent, and are produced by developing the hydration capacity of the low-boiled Mitscherlich type of wood-cellulose, by graduated mechanical treatment in the kollergang

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and beater, to its fullest extent. The principle followed in their preparation is to beat these 'strong' wood pulps between very broad, blunt knives for about twelve hours, with the object of crushing and shredding the fibres rather than cutting them, thereby forcing the water into combination with the cellulose, so that the latter is gradually reduced to a gelatinous mass. It may be assumed that, if any considerable degree of strength and elasticity is to be retained in the paper, care must be taken to avoid the 'dead' beating of the fibres during this very severe treatment, and that the length of the fibres should be maintained as far as possible, although in such extreme cases a certain proportion of non-felting fragments of cellulose cannot be avoided. It may also be assumed that the ideal condition of a hydrated pulp. whatever may be the degree to which hydration is carried, is one in which the fibres, almost unreduced in length, are each surrounded by a gelatinised envelope of their own cell substance, gradually merging towards the interior into unmodified cellulose. In other words, the cementing substance, which is the valuable product of hydration, should be self-contained on the outside of each individual fibre. Only under such conditions could the maximum of strength and pliability be combined with the rattle and consistency of a thoroughly hydrated paper.

The delicate cell-walls of the high-boiled, 'easy-bleaching' wood pulps will not withstand even the most carefully graduated mechanical treatment for a sufficient length of time to give full hydration effects; the fibres tend to break up into short 'dead' beaten fragments which being hydrated are stiff and harsh, and having no length give a weak and brittle paper. But most sulphite pulps of the 'strong' unbleached low-boiled type are sufficiently resistant, and respond admirably to the treatment, yielding wrapping, cartridge and 'grease-proof' papers of excellent strength and quality.

Esparto.—Structurally, this is one of the most valuable of the paper-making celluloses, but its chemical character as an 'oxycellulose' prevents it from taking up the high position to which it would otherwise be entitled. Esparto pulp consists of

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fibres and fibre-like (sclerenchymatous) elements with a small proportion of epidermal cells and hairs. The fibres are practically round in section and exceptionally fine; they are short, but not too short for general purposes, provided their length is not reduced by beating. The rounded section of the fibres prevents them from lying too closely one over another, and gives a combination of bulk and surface, which is most valuable in the manufacture of printing papers for books, illustrations, etc. This property is also valuable for correcting the deficiencies of wood pulp papers in this respect. Moreover, the extreme fineness and consequent flexibility of the esparto fibre confers on the pulp admirable felting qualities for binding the sheet together with a uniform texture; in fact, the esparto fibres, with their extreme fineness, may almost be said to fulfil the functions of fibrillae in wood pulp-esparto mixtures, and to supply the felting properties, in which the stiff, broad wood fibres are deficient. At the same time, the wood pulp fibres, with their greater length and dimensions, impart strength and hardness, when added in small proportions to esparto pulps. From these remarks, it will be seen that an enormous range of characters is obtainable by mixing these two complementary fibres in different proportions, and that wood pulp and esparto stand towards each other in a relationship which in many respects may be compared with that existing between linen and cotton.

The natural hydration capacity of esparto is not great, and since the fibre on account of its short length, is very rarely beaten in the real sense of the term, the hydration is rarely developed. The degree of lignification of the raw material is not very high, and possibly the bulk of the loss entailed in the chemical separation of the purified cellulose does not fall on the cell substance of the fibre elements themselves. These fibre elements are thick-walled in comparison with their diameter, and the pulp is remarkably free from thin-walled cellular residues; all which considerations may be taken as tending to reduce the hydration capacity.

Straw.—Chemically and structurally, straw pulp bears a considerable resemblance to esparto. The proportion of fibrous

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elements, however, is appreciably lower and thin-walled vessels and parenchymatous cells are somewhat frequent. The fibres themselves, though generally rather longer than those of esparto are larger in diameter and thinner-walled in comparison with their diameter. Thus structurally straw cellulose may be regarded as slightly inferior to esparto cellulose, nevertheless, it has a very distinct utility of its own, which is not shared by esparto, and which depends on its great natural hydration tendency. This hydration capacity is probably connected with the circumstances that in the raw state, straw is more highly lignified than esparto, and the isolation of the pure cellulose is attended by far greater losses, a large proportion of which is probably borne by the cell-walls of the fibres, and above all, by those of the delicate non-fibrous parenchyma, leaving the cellulose residues in a more receptive condition. This tendency, whilst rendering straw cellulose unsuitable for bulky, soft, opaque papers, makes it eminently suitable in conjunction with wood pulp, rags or a mixture of the two for thin, hard papers such as are employed for typewriting or 'foreign' note papers. The presence of a proportion of straw imparts a translucency and 'rattle' combined with a slight creaminess of colour which at first sight give an impression of animal sizing. Not infrequently the paper-maker, with questionable propriety, endeavours to enforce this impression of good quality by introducing the word 'linen' into his watermark, even in the entire absence of rag fibres, qualifying it, however, with a euphonious adjective.

We will conclude this chapter with the description of three fibres which can hardly be classed as rag substitutes, and have therefore to be discussed by themselves as partially, or entirely, lignified paper-making elements.

Manila.—This has been described as the strongest of all the paper-making fibres used in this country, a reputation which it probably owes chiefly to its great, but convenient length which is available, if required, without any of the mechanical reduction necessary for the preparation of strong linen pulps. An examination of the section of the fibres (p. 111) shows, however, that the cell-walls are not very thick, and this circumstance, coupled

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with the fact that the crude material is a ligno-cellulose, suggests that the actual strength of the ultimate fibre cannot be so great as that of linen or hemp. In addition to the length of fibre, the strength of papers containing manila is attributable to its extremely high hydration capacity which can be readily developed to any desired extent in the operation of beating, and to which the relative translucency of manila papers may be referred. Manila is seldom boiled and bleached to a pure white cellulose: it is generally treated until the bundles of the ultimate fibres are resolved, and is then mixed with other unbleached strong materials, such as flax and hemp tows, rough rags and 'strong' wood pulps for the manufacture of cartridge, envelope, and wrapping papers and millboards in which strength and toughness form the first consideration.

Jute.—Structurally, this fibre resembles manila in many respects, it is considerably shorter and although useful for general purposes, its shortness prevents it from ever fulfilling the strength-giving functions of manila. Jute is generally boiled with lime for the production of buff-coloured pulps of a lignified character which have been used to some extent to imitate manila papers. The lignification of the jute fibre, and consequent imperfect resolution of the fibre bundles, involves a certain degree of stiffness, in the constituent elements of the paper, to which it imparts a characteristic 'feel' and somewhat 'woolly.' Jute cellulose, fully boiled with soda and bleached, is also utilised as a more or less cylindrical fibre for blending with sulphite wood pulps.

Mechanical Wood Pulp.—Structurally and chemically, this pulp belongs to the lowest order of paper-making materials. It is only used by itself for the manufacture of boards, since the shortness of the fibre fragments, their stiffness and almost total lack of felting properties makes them incapable of holding together a sheet of paper. Mixed with just sufficient long-fibred chemical wood pulp, mechanical wood finds an enormous application for the manufacture of 'news' and other printing papers of the commonest sort. Under the microscope, the elements of mechanical wood pulp may be classified as (1) short-

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ened but otherwise undamaged wood fibres ; (2) shreds of wood fibres torn and mutilated out of all recognition of their fibrous form ; and (3) compound elements, almost as broad as they are long, consisting of shortened fragments of two or more parallel wood fibres held together by the medullary rays. The first two have rather more paper-making value than the last, which can act solely as a filling material. The hydration qualities of mechanical pulp are not very great, nevertheless, differences in this respect occur between the products of different processes of grinding, and depend chiefly on the grain of the stones, the sharpness of the grinding ridges, and possibly also on the temperature of grinding. The 'wetness' of a mechanical pulp would be proportional to the number of mutilated or burst cells, a 'wet' pulp being produced by fine-grained stones with blunt ridges.

A 'wet' short fibred pulp is produced by grinding the wood across the grain, whereas the pulp prepared by grinding along the grain is longer fibred but coarser and possesses very 'free-running' qualities. According to Hofmann, the cross-grain pulp is most suitable for mixing with sulphite pulp for 'news' and common printing papers, whereas the longer but stiffer fibres of long grain pulp do not give a good printing surface. The latter type of pulp is, however, sometimes preferred on account of its 'free' character for the manufacture of thick papers and cardboards consisting entirely of mechanical pulp.

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CHAPTER XIII.

PAPER TESTING.

PAPER may be tested either from the point of view of its physical and mechanical properties, or its material composition.

Before discussing the methods and machines now employed for the more exact testing of paper we will briefly review the properties of the paper as revealed to an ordinary buyer or paper-maker by his senses, and without the aid of any mechanical appliance.

Those who have long experience in 'handling' paper are able to judge quality and value within the space of a few minutes. When a sheet is lifted, the weight, and weight per ream are estimated. The feel between the finger and thumb will reveal not only the character of the surface with regard to its smoothness, but also the 'bulking' qualities. The expert being generally familiar with the process of paper-making will know how, and to what extent, it has been pressed, glazed or calendered, and by what particular process. By holding it between the finger and thumb and shaking it, he gets a knowledge of the 'hardness' and 'rattle' and other qualities that determine the value of a paper, and its suitability. He folds it backwards and forwards between the finger and thumb, rubbing it with the back of the finger nail to judge the folding qualities, an important quality in envelope papers. If sufficiently expert, he may be able to tell whether it is hand-made or machine-made by merely looking at it. By pressing it against the tongue he can say whether it is 'water-leaf' or 'sized' paper, whether 'soft' sized or 'hard' sized. If coloured, he may possibly distinguish in appearance between 'ultramarine' and 'smalts.'

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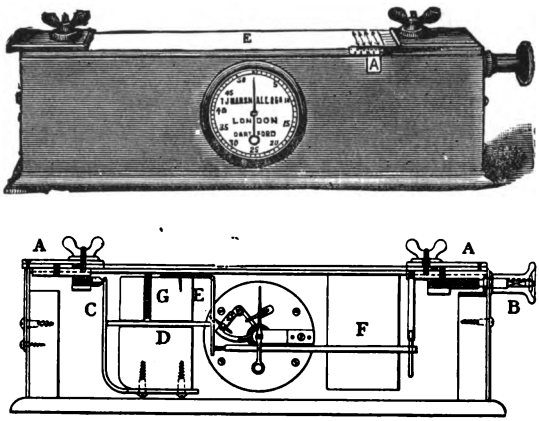
By comparing the two sides he can distinguish the top side from the bottom side; by looking *at* the paper, he can see how the water-marking has been performed. By looking *through* the paper the nature of the beating, the length of the stuff, and the manipulation of the stuff upon the machine can be to some extent judged. By placing a sheet over printed matter he can tell whether it is too opaque or transparent. The tone or shade he can match against known samples.

Such tests are of great utility, and in very experienced hands an approximate estimate can be formed thereon, but they



FIGS. 78 and 79.

lack the fundamental necessity of numerical expression, which must form the basis of any records or comparative tests, hence the necessity of appliances whereby figures expressing certain qualities in paper can be recorded. The tensile strength of a paper can be rapidly judged by means of Marshall's Testing Machine, Figs. 78 and 79, manufactured by Messrs. T. J. Marshall and Co., Stoke Newington.

Strips of uniform width, say 1-inch, are cut, preferably by means of a gauge, and inserted between the jaws, the mill-head is turned steadily by the right hand until fracture takes place.

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The pull in pounds is indicated by the pointer on the circular dial, the stretch or elongation being read off at A (Fig. 78); on reversing the direction of the mill-head the pointer falls back to zero, and the jaws to their original position. For fine papers where any slight irregularity should be detected strips are taken $\frac{5}{8}$-inch wide, for coarse and wrapping papers 2 inches wide, for ordinary work 1 inch wide. For purposes of comparison, results are expressed in terms of 1-inch width, being reduced by calculations to this width when other widths are chosen for the tests. The stretch or elongation is calculated as a percentage of the distance between the jaws.

In cases of dispute the Schopper machine is frequently used, and is recommended for such purposes by the Paper-Makers' Association.

Fig. 80 shows a Schopper machine to be worked by hand; a narrow strip is placed between the clamps and the wheel turned until fracture takes place, the figure for strength being indicated on the graduated segment by a pointer attached to the weighted lever, the stretch being recorded on the smaller segment. For greater accuracy the machine is sometimes driven at uniform speed by power.

In Germany paper-testing is conducted under the elaborate system of the Königl. Techn. Versuchsanstalt, Berlin, of which, through the agency and influence of Prof. Sell and C. Hofmann, a department has been organised exclusively for the work of paper-testing.

The mechanical properties of papers are considered to be represented by data of (1) Tenacity, i.e. actual resistance to tensile strain; (2) 'Elasticity,' or rather elongation up to the point of rupture; (3) Resistance to rubbing.

Tenacity finds a convenient expression in terms of 'breaking length,' i.e. the length of a strip of paper, the weight of which would be equal to its breaking weight. This expression has the advantage that it is independent of the width of the paper, which may therefore be left out of consideration. Further, since the expression 'breaking length' is calculated on the basis of weight and not of dimensions, and since

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paper is made and sold by weight, this expression, as a commercial standard, eliminates and discounts the factors of thickness, bulk, loading, etc., and becomes a common measure

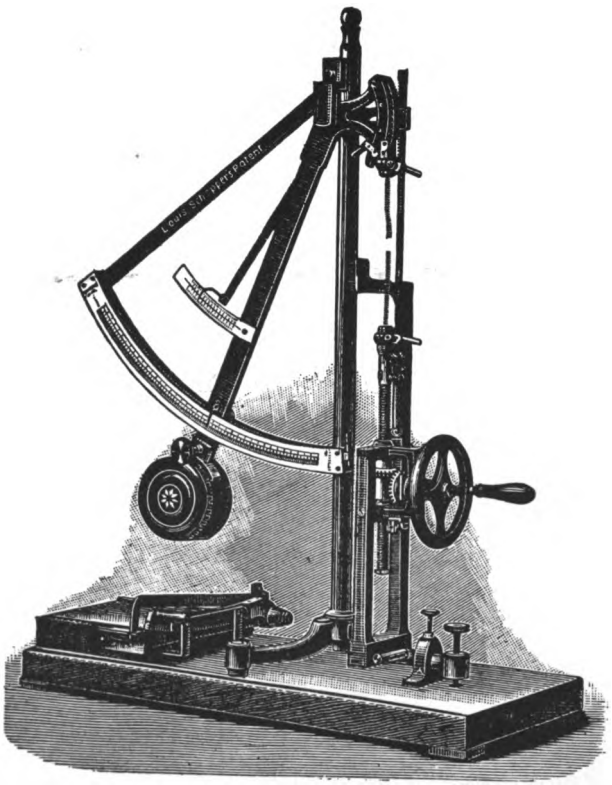

FIG. 80.

for the strength-value of all papers, proportional to the number of 'strength units' per lb. of paper. On this basis Germany has adopted the following 'normal' standards :—

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Class. . . .	1	2	3	4	5	6
(*a*) Mean breaking length (metres) not less than	6000	5000	4000	3000	2000	1000
(*b*) Mean elongation (p.ct.) at fracture not less than . . .	4·5	4	3	2·5	2	1·5
(*c*) Resistance to rubbing .	6	6	5	4	3	1

A further mechanical test, forming a part of the scheme of investigation, is the resistance of the paper to rubbing. This test is altogether an empirical one, as the following brief description will show: A piece of the paper, about 6 inches square, crumpled by successive folding in two directions at right angles, is grasped by the thumb and forefinger of each hand, at a distance of 3 to 4 inches apart. It is then rubbed upon itself across the thumbs a given number of times (seven is the number chosen), and held up to the light. If no holes are visible, the rubbing is repeated. The number of times necessary to repeat the rubbing until holes appear is the measure of resistance. A sufficient uniformity in the results of this test has been observed to make it the basis of a classification of papers, in regard to their resistance to such disintegration. They are divided into the following seven groups, beginning with the lowest:—

0. Extremely weak.
1. Very weak.
2. Weak.
3. Medium.
4. Moderately strong.
5. Strong.
6. Very strong.
7. Extremely strong.

A simple apparatus to determine the loss of strength on folding, devised by Prof. Kirchner, is shown in Fig. 81. It consists of a pinching roll under the weight of which, the strips to be tested, are folded in a regular manner. After folding the strips are broken in a testing machine, and the strength compared with that of the unfolded paper.

An elaborate machine for determining the resistance of paper to repeated folding is shown in Fig. 82.

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It can either be operated by hand or driven mechanically. This machine registers by mechanical means those properties which were previously determined by testing with the hand for resistance to crumpling. The strip of paper is placed under a constant tension of 1 kilo, and is rapidly folded backwards and forwards by the action of a reciprocating connecting-rod until it breaks. In Germany this is the standard machine for the determination of folding qualities, the following 'folding' classes

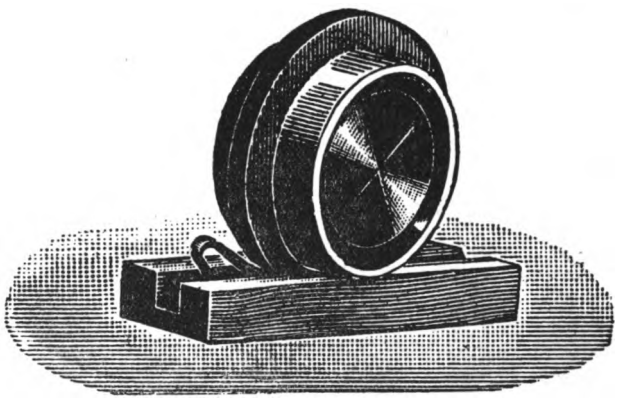

FIG. 81.

being instituted by the Government in January 1904, for normal papers :—

The grades for resistance to crumpling are :—

Grade.	Description.	No. of Double folds.
0	Extremely large	0– 2
1	Very small	3– 6
2	Small	7– 19
3	Medium	20– 39
4	Fairly large	40– 79
5	Large	80–169
6	Very large	190–999
7	Extremely large	1000 and above.

As paper varies in its qualities according to the condition

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of the atmosphere, especially as to moisture, it has been found necessary to maintain a constant percentage of saturation, to record this the hygrometer, invented by Dr. Koppe (Fig. 83), is of service.

This registers on a dial and without calculation, the percentage of saturation; a thermometer by the side records the

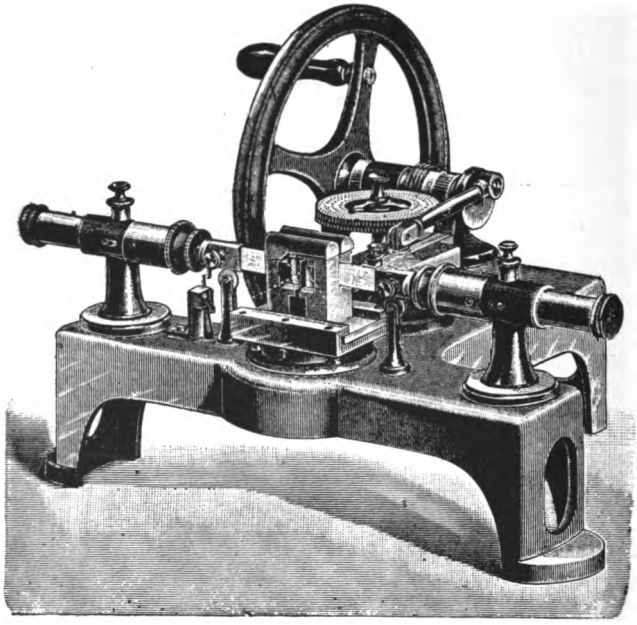

Fig. 82.

temperature. This instrument is used in the Versuchsanstalt in Gross-Lichterfelde West, where the paper is always tested under a uniform saturation of 65 p.ct.

In order to determine the thickness of paper which needs for some purposes to be recorded with great accuracy, Schopper's dial micrometer is of service. (Fig. 84.)

It is used in works where any slight variation has to be

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detected; it records on the dial the thickness to the 1000th of a mm.

Fig. 85 shows a portable hand micrometer.

In order to prevent undue pressure on the surface, a friction clutch is often introduced by means of which all papers can be tested under uniform pressure, otherwise irregular readings are recorded, due to the paper being, more or less, compressed.

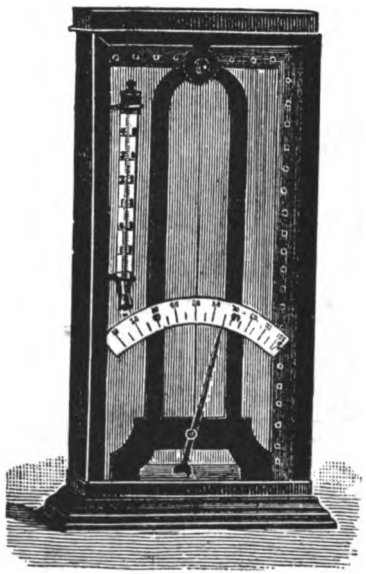

FIG. 83.

A system of testing papers has recently been introduced, known as the C.B.S. units, by which method a large range of commercial papers have been investigated.* A steel punch with a sharp edge, constructed like a leather punch, and producing discs of exactly 1000 square mm. in area, is forced by

* 'The C.B.S. Units and Standard Paper Tests'; an Essay towards establishing a normal system of paper testing, by C. F. Cross, E. J. Bevan, Clayton Beadle, and R. W. Sindall. London.

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means of a hammer through the paper placed on a firm block of wood lined with lead, the sheet being preferably so folded as to produce 10 discs in one operation. The discs are measured by means of a micrometer and weighed, the weight in grammes divided by the thickness in mm. gives directly the grammes per c.c. of paper or the apparent specific gravity. The percentage of ash is determined in the paper and the amount is calculated for the weight contained in the 10 discs; this when deducted from the weight of the discs gives the weight of fibrous material which can be calculated into grammes per c.c.

FIG. 84.

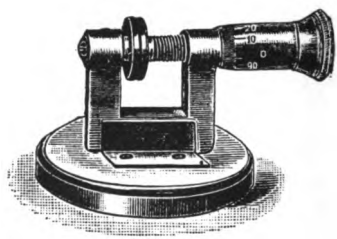

FIG. 85.

To arrive at the volume occupied by the fibre, this figure is divided by the specific gravity which is taken at 1·5. If the amount of ash in the paper is very small, the percentage of air space is obtained by deducting the fibre volume from 100. If the ash is more than 1 p.ct., its volume may be taken into consideration; this is done in the manner above indicated for percentage of fibre volume, but on the assumption that mineral loading has a specific gravity of 2·5. This gives a record of the percentage by volume of fibre, mineral matter, and air space.

As bulk in this sense is measured by air space, and is in inverse ratio to the fibre density, the ratio of total volume

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to fibre volume (when fibre = 1) is taken as a figure expressing the relative 'bulking' qualities. Commercial papers are found to vary from 70 to 20 in percentage of air space, and the figure for bulk to fall between 1·2 to 3·4. In the C.B.S. units, when testing for strength, the cross section of the sheet of paper is taken into consideration, the figure for strength being expressed in grammes per square mm. of sectional area, thus directly comparing the strength of paper in its dimensional relations with that of other structural materials which usually find expression in similar terms

A knowledge of the bulking qualities, air space, volume percentage, etc., is of service in comparing papers such as 'feather-weight,' blotting, filtering, as well as very thin paper, such as India and Bible papers, and dense papers such as parchment, bank notes, etc. Such tests have their utility for all classes of paper, and we commend this system to our readers as affording a useful basis of research as well as for recording obviously commercial qualities.

For testing blottings for absorbency, an instrument, the 'Bibliometer,' has been devised whereby a strip is lowered vertically downwards into a trough containing water or ink, the rate of rise being indicated by an attached scale, this is generally recorded in mm. per minute. The instrument is manufactured by Messrs. T. J. Marshall and Co., of Stoke Newington. (See Fig. 86.)

Determination of Composition of Papers.

The analysis of a paper naturally divides itself into two parts: (*a*) The determination of the nature of the fibrous material of which it is composed; and (*b*) the identification of such adventitious substances as size and filling material.

(*a*) This again is divided into two sets of observations—microscopical and chemical.

A fragment of the paper is soaked for some time or boiled for a short time in dilute alkaline solution, and is then carefully teased out with a pair of needles, and the fragments laid on a

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glass slip with a drop of diluted glycerin. A cover-glass is then laid on and lightly pressed down so as to spread the fibres in a thin layer.

The microscopical features of the different fibres have been already described, (Chapter IV.) and it is only necessary now to summarise the chief characteristics of the more important materials.

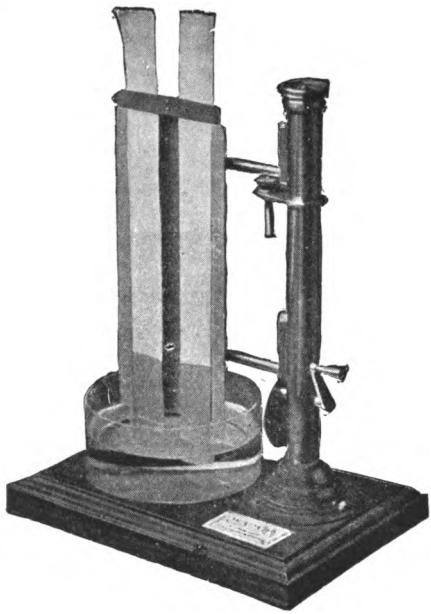

FIG. 86.

Cotton.—Flat riband-like fibres, frequently twisted upon themselves. The ends generally appear laminated. The fibres are frequently covered with numerous fine markings (see Frontispiece).

Linen.—Cylindrical fibres, similar to the typical bast fibre (see Fig. 6). The ends are frequently drawn out into numerous fibrillæ (see Frontispiece).

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Esparto.—Esparto pulp consists of a complex of bast fibres and epidermal cells. These serrated cells are, as has been already pointed out, characteristic of esparto, straw, and similar fibres. Certain differences exist between those of esparto and straw, and even between the different species of straw, which enable the microscopist to identify their source. The most characteristic feature of esparto pulp is the presence of a number of the fine hairs which line the inner surface of the leaf (*e*, Fig. 10), some of which invariably survive the boiling and washing processes, although the greater portion passes away through the wire-cloth of the washing engines. The presence of these hairs may be taken as conclusive evidence of the presence of esparto.

Straw.—Straw pulp very closely resembles esparto pulp in its microscopical features. The hairs above alluded to are, however, absent. On the other hand, a number of flat oval cells are always present in paper made from straw (*b*, Fig. 13). It should be borne in mind, however, that bamboo and similar pulps also contain these cells.

Wood (Chemical).—Flat riband-like fibres, showing unbroken ends (see photographs, Frontispiece). The presence of the pitted tracheids (Frontispiece, and Fig. 15) is eminently characteristic of pulp prepared from coniferous wood. The fibres of other woods are less obviously characteristic. (See p. 112.)

Wood (Mechanical).—Mechanical wood-pulp may be recognised by the peculiar configuration of the torn ends of the fibres, and from the fact that the fibres are rarely separated, but are generally more or less agglomerated (see Frontispiece). Pulp from coniferæ of course shows the pitted vessels already referred to. They are usually more distinct than in 'chemical' wood-pulp. Occasionally fragments are to be met with connected together with portions of the medullary rays.

The identification of the ligno-cellulose is rendered very certain by previously staining the specimen with a basic-aniline dye, or with the phloroglucol reagent (p. 87), or with a solution of a salt of aniline or dimethyl p. phenylene diamine.

The microscopical examination of a paper is a matter of

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very great difficulty, and one requiring much practice. The student is recommended to study closely for himself the microscopical features of pulps obtained from authentic specimens.

A fair measurement of the relative proportion of the various fibres present in a paper can be obtained from a careful microscopical examination.

Vetillart* was the first to maintain that a quantitative determination within a fair limit of accuracy is possible.

The degree of accuracy attainable depends first upon the kind of mixture under examination, and secondly, upon the experience of the observer.

In examining the paper under the microscope, it should be observed whether the fibres appear as fragments, or whether they consist of whole cells in which the natural ends are preserved.

Cotton and linen, owing to the great length of their ultimate fibres, yield, when beaten, fragments showing where the fracture has taken place. From the appearance of this fracture it is possible to ascertain how the beating operation has been conducted. If the beater knives have been sharp, or have been let down to the bed-plate too quickly, the fractures will appear as clean cuts, whereas when the operation has been otherwise conducted, the fraction will appear ragged and drawn out. The bearing of this on the strength of the finished paper is considerable.

Esparto and straw, with ultimate fibres not exceeding 1–2 mm., should, in the majority of cases, appear as whole (bast) fibres with two tapered ends; the beating, when properly conducted, being confined merely to the separation into these ultimate fibres.

(*b*) For the chemical identification of the fibres in writing and printing papers, the most useful reactions are those with aniline sulphate solution. The fibres (celluloses) of the rag and

* Études sur les Fibres Végétales Textiles, Paris, 1876 (Firmin-Didot).

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wood groups give no reaction, but straw and esparto celluloses and mechanical wood-pulp can be identified by its means. The authors have found that when a paper containing straw or esparto is treated for some time with a boiling 1 p.ct. solution of aniline sulphate, a red colour is produced. Esparto gives the reaction with greater intensity than straw. In this way, the presence of a very small quantity of these pulps can be detected with certainty. Since esparto and straw cellulose give large yields of furfural in boiling with hydrochloric acid of 1·06 sp. gr., a determination of furfural gives a close approximation to the proportion of these celluloses in a paper containing only linen and cotton celluloses in addition. The percentage is obtained by multiplying the furfural number by 8.*

Mechanical wood-pulp, when treated with a solution of aniline sulphate, develops, even in the cold, a deep yellow colour. If a paper containing mechanical wood-pulp so treated be examined under the microscope, the fragments of wood will be found to be deeply stained, whereas the other fibres remain colourless or nearly so. It must be borne in mind that cellulose obtained from lignified fibres, if the boiling and bleaching processes have not been carried sufficiently far, will give with aniline sulphate a more or less intense yellow colouration. Various other reagents have been suggested for the identification of mechanical wood-pulp, all based upon the production of a colour with lignone. Of these, the most important is the solution of the coal tar base, dimethyl p. phenylene diamine, the reactions of which have been previously described.

The reaction of lignone with chlorine and sodium sulphite solution already referred to (p. 87) may also be made available for the detection of mechanical wood-pulp in a paper. Imperfectly boiled or bleached pulps sometimes give this reaction faintly.

Quantitative Estimation of Mechanical Wood-pulp.—The determination of the amount of mechanical wood-pulp present in a paper is sometimes a matter of some importance, and it is

* For details of furfural estimation, see 'Cellulose.'

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also a matter of some difficulty. A general idea of the amount present can be obtained by observing the depth of the yellow colour produced with aniline sulphate or the intensity of the magenta reaction with chlorine and sodium sulphite. Wurster's colour reactions (supra) are more pronounced and the quantitative findings based upon them are generally accepted as affording a sufficiently close approximation. Test papers containing the diamine base together with a scale of colours corresponding to varying percentages of the ligno-cellulose, are obtained from Schuchardt of Görlitz (Germany). It is also possible to calculate approximately the percentage from the percentage of cellulose contained in the specimen. Mechanical wood-pulp (pine) may be taken to contain 60 p.ct. of cellulose. If, therefore, a paper ascertained to contain a pure cellulose in addition to this constituent, yield 75 p.ct. of cellulose on the ordinary test, it may be assumed that about 62·5 p.ct. of mechanical wood-pulp is present.

The authors have proposed a method of estimating the amount of mechanical wood-pulp present in a paper, based upon the absorption of iodine in definite proportions by wood in a finely divided state, under strictly regulated conditions (see p. 59). The paper is carefully reduced to a fine pulp and is then left in contact with a standard solution of iodine in potassium iodide. At the end of twenty-four hours, the amount of free iodine is determined by titration with sodium thiosulphate, and by deducting this from the amount originally taken, the amount absorbed is ascertained. As this amount, under strictly comparative conditions, always corresponds to a definite amount of mechanical wood-pulp, the amount present can be readily calculated.

Another method which can be made to yield useful results, if carefully standardised, is based on the determination of the quantity of hydrochloric acid which is produced by the action of chlorine gas on the moist ligno-cellulose (see p. 57). The production of the chlorolignone compound there described is accompanied by that of a quantity of hydrochloric acid which appears to be a specific constant of the type of ligno-cellulose in

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question (see Cross and Bevan, 'Cellulose' p. 193). The paper is prepared by boiling 10 grm. of the sample for a few minutes in a 1 per cent. solution of sodium carbonate. The liquid is poured off, the residue is acidified with a few drops of acetic acid and washed with hot water until neutral. The paper is then thoroughly pressed and exposed in the damp state to the action of washed chlorine gas, care being taken that a thorough and uniform access of the gas is ensured. After chlorination is complete, the excess of chlorine is allowed to escape by short exposure to the air, and a known volume of water is added. The quantity of hydrochloric acid in the extract is then determined by titration with normal soda. The results are calculated by reference to those obtained in the case of pure mechanical wood-pulps of the same type. The following table shows the acid equivalent of 1 grm. of various samples of pulp expressed as c.c. of normal alkali.

Pure mechanical, 1 grm.	. .	4·4 c.c. normal alkali.	
Aspen ,, ,,	. .	3·5	,, ,,
Sulphite pulp (unbleached), 1 grm.		0·46	,, ,,
Sulphite ,, (bleached)	,,	0·03	,, ,,

2. *Loading, Sizing Materials, etc.*—The determination of the amount of loading material in a paper has been already described (p. 224). The identification of the material can only be arrived at by a careful chemical analysis. The principal loading materials are china-clay and pearl-hardening (calcium sulphate), and in coated or 'art' papers, barium sulphate. The ash from a paper containing china-clay is insoluble in boiling dilute hydrochloric acid; that from paper containing calcium sulphate is soluble: the solution on cooling deposits long needle-shaped crystals of $CaSO_4 2H_2O$ and gives with barium chloride a copious precipitate of $BaSO_4$ (barium sulphate) insoluble in acids, and with ammonia and oxalate of ammonia a precipitate of calcium oxalate. To examine for barium sulphate the ash is fused with a mixture of sodium and potassium carbonate. The mass is boiled out with water.

The presence of starch in a paper can be readily ascertained by its behaviour with a solution of iodine. If starch be

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present the well-known blue colour of the compound of iodine and starch will be produced. The determination of the amount of starch present is a matter of some difficulty, the details of which are somewhat beyond the scope of the present work. It is based upon the conversion of the starch into sugar, and the estimation of the latter with Fehling's solution.

The authors have investigated the removal of starch by the action of saliva. The amylolytic action of this secretion is favoured by a slightly alkaline reaction, and a temperature of 30°–40° C. The paper to be tested is treated with boiling water and after cooling to 40° a little sodium bicarbonate is added (to slightly alkaline reaction), then a small quantity of saliva. With this it is digested 4–5 hours at 30°–40° and then washed. The starch is estimated by the loss of weight sustained.

The nature of the material with which a paper is sized may be ascertained in the following way :—

The sample, cut up into small fragments, is warmed for a few minutes with pure alcohol containing a few drops of acetic acid. The alcohol is allowed to cool, and is then poured into four or five times its bulk of distilled water. If any precipitate or cloudiness is produced, it indicates that the paper has been sized with rosin. The alcohol dissolves the rosin, which, being insoluble in water, is thrown down on dilution. Glacial acetic acid may be used as the solvent in place of alcohol.

The paper after treatment with alcohol should be boiled for some minutes with water : the solution allowed to cool, and then filtered. To the filtrate a few drops of a solution of tannic acid are added, when, if the paper has been sized with gelatine, a white curdy precipitate will be formed.

The estimation of the amount of sizing material in a paper is a very complicated process and one which demands considerable chemical experience for its proper conduct.

The amount of gelatine present is best ascertained by determining the amount of nitrogen present by combustion with soda-lime, or preferably by the alternative Kjeldahl process, and from this, calculating the amount of gelatine. Pure gelatine contains 18·16 p.ct. of nitrogen (Muntz). The

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comparison of one paper with another with a view to ascertain the relative degree of sizing, is usually performed in a more or less rough and ready way by moistening the samples with the tongue for a certain time, and noticing the degree of transparency produced, which is of course inversely to the degree of 'hardness.' A more accurate method consists in placing a drop of a mixture of alcohol and water containing some colouring matter in solution and determining the time necessary for the colour to make its appearance on the other side. In this way more trustworthy comparisons can be made.

Colouring Matters.—The chemical characteristics of the chief colouring matters have been already described. 'Mineral' pigments will be obtained in the ash, in some cases without chemical change (smalts, iron oxides, etc.), in other cases in the form of the characteristic constituent of the original pigments. Thus the prussian blues leave a residue of iron oxide; the chromates may be more or less 'reduced' to chromic oxide. The coal-tar colours and soluble dyes are recognised by characteristic reactions, for which the special text-books dealing with the subject must be consulted. (See p. 231).

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CHAPTER XIV.

GENERAL CHEMICAL ANALYSIS FOR PAPER-MAKERS.

A KNOWLEDGE of the methods usually employed for the qualitative and quantitative analysis of the various chemical substances met with in paper manufacture is of considerable importance. The scope of this work will not allow us to enter fully into the necessary details of manipulation; for these the reader is referred to standard works on analysis: we will merely indicate the methods.

Lime.—In its commercial forms contains in addition to the active calcium oxide, water and carbonic acid, in combination with lime, and substances insoluble in acids, derived partly from the original limestone, partly from the coal used in 'burning' it.

Magnesian limestones yield a lime containing, of course, magnesia.

These facts indicate the methods to be pursued by the analyst in valuing a sample of lime. Water and carbonic acid may be estimated jointly by the loss of weight on igniting to a white heat in a platinum vessel till constant. Earthy impurities such as sand can be determined by treating the lime with a dilute acid in slight excess, filtering off and weighing the insoluble matter. For an exact determination of silica, alumina, iron oxide and magnesia, the usual systematic separation must be followed.

On account of the heterogeneous nature of lime the main point of its valuation is the obtaining of a fair average sample for analysis. For this purpose, the following method may be employed :—

A large sample, from 1 to 10 kilos, according to the

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delicacy of the balance, is taken from the bulk and is broken up roughly with a hammer. The sample is then weighed in a shallow iron vessel, and is copiously sprinkled with water. The heat, which is then developed on slaking, drives off the excess of water in the form of steam, and the lime is transformed into a dry powder of the hydrate which is weighed again when cold. The ratio of the weight of the hydrate to that of the original quicklime serves as a basis for the calculation of the analytical results. The powdered hydrate is then thoroughly mixed, and a small average sample is bottled off for analysis.

In actual practice it is usual to estimate the lime by a direct volumetric method; a standard solution of oxalic acid being added to the lime previously slaked and brought to the condition of 'milk of lime.' As an indicator, phenolphthalein is used. The reaction is carried out in a stoppered bottle, which is vigorously shaken from time to time. The oxalic acid solution is added until the pink colour of the phenolphthalein is discharged.

An alternative method for the determination of the caustic lime is as follows: 5·6 grm. of the sample are weighed out and placed in a 200 c.c. flask, together with about 100 c.c. of water and 40 grm. of powdered sugar. The mixture is digested at the ordinary temperature with occasional shaking for 2 hours. The caustic lime is soluble in the sugar solution and the contents of the flask are diluted to 200 c.c. The liquid is then filtered through a dry filter and 10 c.c. of the clear filtrate are titrated with normal hydrochloric acid. The number of c.c. of acid used × 10, gives the percentage of CaO in the sample.

Caustic Soda, Soda Ash, Recovered Soda, etc.—These substances are always valued by the amount of real alkali (Na_2O) that they contain, which is determined by titration with a standard acid.

In testing recovered soda, it is necessary to *boil* the finely powdered ash for some time with water; unless this be done, the amount of alkali will probably be under-estimated, as part of the soda is present as a difficultly soluble silicate.

It is sometimes desirable to determine the amount both of

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sodium hydrate and carbonate in a sample of alkali. For this purpose an excess of a solution of barium chloride is added to a solution containing a known quantity of the substance under examination, and the mixture made up to a definite volume. It is then filtered, and an aliquot portion of the filtrate titrated with standard alkali. The filtrate contains only the alkali that was originally present as hydrate, the carbonate of soda having formed with the barium chloride, insoluble barium carbonate, and sodium chloride.

A more usual and rapid method consists in titrating a solution of the sample with standard acid in presence first of phenolphthalein and then of methyl orange. The difference between the two values × 2 indicates what portion of the total alkalinity is due to carbonate.

Bleaching Powder.—The value of bleaching powder depends upon the amount of 'available chlorine' that it contains. This is determined by means of a standard solution of arsenious acid. The standard solution is prepared by dissolving pure arsenious oxide (As_2O_3) in sodium carbonate solution. To test the powder, a quantity, say about 5 grm., is taken, and is carefully ground up in a mortar with a small quantity of water; more water is then added, and the coarser particles allowed to settle for a few seconds. The milky liquid is then run off into a graduated flask; the residue is again ground up with water, and the operations repeated until the whole of the powder is transferred to the flask. The liquid is now diluted to 1 litre, carefully shaken, and an aliquot portion withdrawn as quickly as possible. It is necessary to take both the soluble and insoluble portions in order to obtain uniform results. Standard arsenious acid solution is now run in until the solution ceases to produce a blue colour with iodide of potassium and starch papers.

A very rapid and satisfactory method is that of causing the bleaching powder to liberate its equivalent of iodine from potassium iodide in presence of hydrochloric acid using sufficient excess of the iodide to dissolve the liberated iodine completely. The iodine is then titrated in the usual way with a standard solution of sodium thiosulphate.

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The method of estimating the amount of available chlorine in bleaching powder by determining the quantity of ferrous sulphate it is capable of oxidising is fallacious, as by this means calcium chlorate is included in the result.

In bleaching powders of low strength this test becomes, however, of value as a measure of the spontaneous decomposition of the powder causing loss of 'available chlorine.' The 'chlorate' strength may be taken as the difference between the numbers for total oxidising chlorine and available or hypochlorite chlorine.

Bleaching powder should contain about 35 p.ct. of available chlorine, but the percentage frequently falls below this amount, especially in warm weather.

Great care should be exercised in the sampling of bleaching powder, as indeed of all chemicals, in order to insure an average result. Small portions should be taken from different parts of the bulk; the whole should then be carefully mixed, and, if necessary, reduced to powder. Portions of the mixture should be taken, pounded, and again thoroughly mixed.

If this process be repeated once or twice, a perfectly uniform sample will be obtained.

Alum, Sulphate of Alumina, Alum Cake, etc.—The points to be considered in an examination of such of these products as are perfectly soluble in water are (1) the percentage of alumina contained in them; (2) the percentage of iron, and (3) the amount of free sulphuric acid present.

(1) The alumina is estimated as such by precipitation with ammonia. Ferric oxide is also thrown down with alumina, and must therefore be deducted from the amount of the mixed oxides obtained.

(2) The percentage of iron oxide present is determined in the following way. A considerable quantity of the sample under examination is dissolved in water, and to the boiling solution a large excess of caustic potash solution is added. The caustic potash precipitates both the alumina and ferric hydrates: the former, however, re-dissolves. The solution is filtered, and the precipitate of ferric hydrate washed,

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dissolved in dilute hydrochloric acid, and re-precipitated with excess of caustic potash. It is again thrown on to a filter, washed, re-dissolved in hydrochloric acid, and again re-precipitated with ammonia. In this way it is obtained free from alumina.*

An alternative method, to be recommended when the iron is present in larger proportion, is the volumetric process with permanganate: the ferric being reduced to ferrous oxide by reduction with zinc in presence of acid, the latter being then quantitatively re-oxidised by the titrated permanganate solution.

(3) *Free Acid.*—This can be estimated indirectly, i.e. by estimating the alumina and ferric oxide, calculating the amount of sulphuric acid necessary to combine with them, and deducting this from the total amount of sulphuric acid estimated. In the case of alum it is of course necessary to make due allowance for the sulphate of potash or ammonia present. The sulphuric acid is estimated as barium sulphate in the usual way.

An approximate method of estimating free acid consists in digesting a weighed quantity of the finely powdered sample in strong alcohol. The alcohol dissolves away the free acid, which can be estimated in the solution by means of a standard solution of alkali.

Free acid can be detected by means of a solution of Congo-red which is turned blue with free acid, but not with pure sulphate of alumina.

Another indicator which is sensitive to free acid, but is not changed by the pure sulphate is made by extracting 1 part of logwood with 3 parts of boiling water, and adding 1 part of alcohol to the decoction after cooling.

Insoluble Matter is present in greater or less proportion in many of the 'alum cakes' of commerce. Such constituents are of course destitute of 'alum value.' They are estimated by

* For a method of estimating minute quantities of iron in alums, see 'Journ. Soc. Chem. Ind.,' April 1887, p. 276.

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boiling out the sample with water; collecting, washing, drying, and weighing the undissolved residue.

Sizing Test.—Griffin and Little recommend a direct measure of the sulphate of alumina in terms of rosin size precipitated. The following are the practical details of the test as given in their 'Chemistry of Paper-making,' pp. 381, 382.

A standard size solution is prepared by dissolving about 25 grammes of good ordinary rosin in about 250 c.c. of strong alcohol. The solution is then filtered from insoluble matter, and diluted with a mixture of 500 c.c. of strong alcohol, and 300 c.c. of water to nearly 1000 c.c. A little phenolphthalein in solution is then added, and standard soda solution added drop by drop, shaking after each addition until a faint pink tinge is observed in the solution. This shows that all the rosin acids are combined with soda, and that the solution is one of neutral resinate of soda, or neutral rosin size. The solution is now to be made to 1000 c.c. with the diluted alcohol mentioned above, and if not entirely clear, filtered again or allowed to stand until it settles clear. The clear alcoholic solution constitutes the standard size solution.

The value of this solution is next to be determined, best by means of a solution of pure crystallised ammonia alum, one part of which alum we have found to precipitate 2·46 parts of neutral rosin size.

For this purpose, the clear colourless crystals should be coarsely crushed in a mortar, and the resulting powder pressed between two sheets of filtering paper to remove any accidental moisture. Five grammes are then carefully weighed and dissolved to 500 c.c. Each cubic centimetre of this solution will then contain 0·01 gramme of alum.

Two burettes are next filled, one with the size solution, and one with the alum solution.

A flask of 150 to 200 c.c. capacity is filled about two-thirds full of water, and 20 c.c. of the size solution is run into it from the burette. The alum solution is next run in, a few drops at a time, the mouth of the flask being closed with the thumb and the flask vigorously shaken after each addition of alum, and

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allowed to rest until the flocculent precipitate formed has risen clear, which takes but a few moments. The addition of the alum solution should be continued until the precipitate on rising leaves the solution entirely clear, without the slightest trace of milkiness or opalescence.

The number of cubic centimetres of alum × 0·01 equals the amount of ammonia alum required to precipitate the size in the 20 c.c. of standard size employed. This multiplied by the factor for ammonia alum, as above, equals the quantity in grammes of neutral size in 20 c.c. of the standard solution.

The actual test of an alum is performed in exactly the same way; a solution of 5 grammes of the alum to 500 c.c. being employed, and, if necessary, filtered through a dry filter before titrating. 20 c.c. of the standard size solution are always employed, and the actual amount of neutral size it contains having been determined as above, it is easy to calculate from the data given by the titration the amount of size which one part of the alum tested will precipitate.

This test, as is evident, gives the absolute precipitating power of the alum, and does not discriminate between sulphates of alumina iron, or other metallic oxides which may be present, or free acid, all of which have the power of precipitating size.

Antichlor, Sodium Thiosulphate, Sodium Sulphite, etc.—Sodium thiosulphate can be estimated by means of a standard solution of iodine in potassium iodide. The operation should be performed in dilute solution (see p. 204).

The same solution serves also for the estimation of sulphurous acid in sodium sulphite and similar compounds.

Starches.—After having made a careful microscopical examination of the sample, it should be examined for water by drying at 100° C., and for mineral matter by igniting in a platinum crucible and weighing the residue. The water should not exceed 18 p.ct. and the ash 0·5 p.ct. The samples should be carefully examined for insoluble matter by dissolving in water and filtering. It is also useful in comparing different samples of starch to convert the specimens into pastes, under exactly similar conditions.

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When perfectly cold, the 'stiffness' of the pastes should be compared. This may be done by noting the relative resistance to weights placed upon their surface. Information on this subject is contained in a paper by W. Thomson in the 'Journ. Soc. Chem. Ind.,' March 1886.

The identification of starches by means of their microscopical appearance is tolerably simple, as each particular kind possesses individual characteristics.

Gelatine.—Samples of gelatine should be examined for water and ash. The water should not exceed 16 p.ct. and the ash 2·7 p.ct. The relative strength of the jellies formed with water should also be compared. This may be done in the way indicated above for starches.

Raw materials intended for the preparation of gelatine may be similarly examined. They yield the whole of their gelatine on heating with water. The effect of prolonged heating on solution of gelatine should be borne in mind. The amount of residue left after treatment with water should be carefully determined.

Soaps.—The soaps most suitable for use in paper-making are those known as curd and mottled, the former being chiefly used for the fine qualities. They should be carefully examined for free alkali and unsaponified fat. Full descriptions are contained in Lant Carpenter's 'Treatise on Soap-making.'

Dyes, Pigments, Loading Materials, etc.—These substances are best examined from a physical and tinctorial point of view, by comparison with specimens of undoubted purity and excellence.

The chemical examination is both difficult and somewhat misleading. A microscopical examination will often throw much light on their composition.

For comparing the tinctorial power of pigments, weighed quantities should be ground up with starch or some other white powder. In this way the comparison of the intensity of colour is much facilitated.

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CHAPTER XV.

SITE FOR PAPER-MILL, WATER-SUPPLY, WATER PURIFICATION, ETC.

In choosing a spot on which to build a paper-mill, the manufacturer has to take into consideration several very important circumstances. Chief of these is the necessity for having a large supply of water at command. Not only is a large quantity needful, but it should be free from impurities, such as suspended matter and soluble iron. The former, it is true, can be removed by settling and filtration; the latter cannot, and is liable to affect injuriously the colour of the paper. Again, as a question of economy in working, it is advantageous to have convenient water-power; therefore, for this as well as for the former reason, paper-mills are usually situated on the bank of a stream. In choosing such a site paper-makers are probably also influenced by the fact that it affords a ready means for the removal of impurities. In properly conducted mills, where suitable apparatus is employed for evaporating the liquors in which the raw material has been boiled, the stream should not be polluted to any very great extent by the mill effluents. Generally speaking, the greater the pollution, the more are valuable materials being lost to the manufacturer. It is obvious that the site for a mill should also be chosen with reference to its proximity to means of transit for the raw and manufactured materials.

Consumption of Water.—It is hardly necessary to emphasise the fact that the consumption of water per ton varies with each class of paper, even when made at the same mill and from the same class of material, notwithstanding that the pre-

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liminary treatment of raw materials (e.g. esparto) requires a fairly fixed and known quantity. The subsequent treatments, more particularly that on the machine, require more or less water, according to the thickness and quality of the paper to be produced; and further, the general arrangement of machine and disposition of the 'save-all' directly influence the amount of water used. The maximum consumption of water is in the manufacture of rag paper, where cleanliness is of primary importance; the consumption is relatively large in all the stages of preparation and also on the machine, and may be as high as 150,000 gallons per ton. The other extreme is in the manufacture of 'news' where the stuff first comes in contact with water in the breaker or beater. We put the consumption of water with 'news' at somewhere between 7000 and 12,000 gallons per ton. With a 'wood' paper where the cellulose has to be bleached, it would be greater in proportion as the bleached wood in the furnish increases. The figure for esparto papers ranges between 25,000 and 50,000 gallons per ton. This is influenced by the amount of mineral and 'broke' as well as by other questions already referred to.

It is necessary to note that the water consumption for dilution of the stuff would amount to about 22,400 gallons per ton on the assumption that the stuff as it passes on to the wire contains about 1 p.ct. of fibre. This must have been an average minimum in the early days of the paper machine, before the water of the save-all was utilised. Taking this and other economies into account, the consumption of water must have been at least 18,000 gallons per ton in excess of what it is at present for all qualities.

The water used in steam raising is best got at by consulting the coal book, which should give the coal consumption per week. The calculated quantity of coal per ton of paper must be multiplied by the evaporating efficiency of the coal. As a general basis of computation we may take 8 lb. water evaporated per 1 lb. coal consumed in the furnaces. The water consumption for any class of paper being necessarily variable, we give one or two concrete instances of actual measurement

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showing the distribution of the consumption over the several processes.

	Water required to make a ton of linen Bank paper. Gals.		Per cent. on Total.
For boiling, etc., 14 cwt. × 2 of rags	5,500	=	5·0
Washing in engine for 2½ hours at 70 gallons per minute: 70 gallons by 150 minutes by 5 engines	52,530	=	5·0
Washing out bleach for 15 minutes at 50 gallons per minute for 5 engines	3,750	=	3·9
Water emptied with 5 beaters, 1200 gallons	6,000	=	6·3
Water run in at auxiliary strainer (500 gallons per hour for 8 hours)	4,000	=	4·2
Water put in as spray on knotters	1,840	=	2·0
Water used at suction boxes, couch roll, and spray pipes for wash rolls, etc.	20,000	=	21·2
For washing 9 cwt. of skins for size	7,000	=	7·2
	95,640		100·0

To the above may be added 10,000 to 15,000 gallons used in steam raising.

As an example of another class, we give a mill making printings of the following furnish : 47 p.ct. straw and 47 p.ct. esparto and 6 p.ct. of loading. The quantity of clean sorted fibre to be treated is esparto, 24 cwt., and straw, 25 cwt. In esparto boiling 790 gallons of liquor and 600 gallons from condensed steam are used, the grass being washed in a series of tanks consuming in all 2500 gallons ; the straw boiling (wheat or oats) requires 1000 gallons of liquor at 10° Tw., and 700 gallons of water as steam ; washing the straw consuming 2600 gallons.

The pulps in potcher required for washing (before the bleach was run in) 5000 gallons for esparto and 6000 for the straw ; net dry weight before bleaching 11 cwt. esparto pulp to 11½ cwt. of straw. The water taken by bleach and the

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presse-pâte amounted to about 4000 gallons for each class of material, and for beaters above 1800 gallons each. The amount of half-stuff dry weight after bleaching was about 1 ton. The fresh water consumed on the machine was approximately 4400 gallons, the rest being got by using the back-water. A quantity of back-water was also used in furnishing the beaters. The finished paper amounted to about 21 cwt., including loading. Thus we have 1 ton net weight of good paper, after allowing 5 p.ct. for waste and 'broke,' most of which was repulped and used again.

SUMMARY OF ABOVE.

	Gallons of water used per ton of Paper.		Per cent. on Total.
Boiling	3,090	=	7·7
Washing	5,100	=	12·8
Washing in Potcher	11,000	=	27·5
Presse-pâte	8,000	=	20·0
Beaters	3,600	=	9·0
Machines	4,000	=	10·0
Steam boilers, clay, dye and jets for machines, etc.	5,210	=	13·0
	40,000		100·0

Water for steam-raising not given.

Another example for esparto papers, leaving out the minor items :—

	Gallons of water ger ton of Paper required.		Per cent. on Total
Soda recovery and esparto boilers	3,000	=	7
Potchers and presse-pâte	10,000	=	25
Beaters	6,000	=	15
Machine	13,000	=	33
Water as steam	6,000	=	15
Sundry purposes	2,000	=	5
	40,000		100

Water for steam-raising not given.

Location of Mill.—The location of most of the old-established mills in this country has been determined by the water supply available. Water power was indispensable before

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the introduction of steam; hence the necessity of being on a river. Many mills still use what water power there is available.

A further reason for proximity to a stream is the necessity for a copious supply of water of good colour and free from impurities, such as dissolved iron, suspended matter and other substances liable to spoil the paper. A stream also provided a means for the discharge of waste or effluent waters, although, through force of circumstances, many mills are now connected with a sewer, where such is available, into which they discharge the worst of their effluent, the remainder being treated to remove impurities so that an effluent can be discharged into the stream sufficiently pure to satisfy the requirements of the authorities. Esparto mills, of course, evaporated their liquors for recovery of alkali; only a small fraction, say 1·0 p.ct. being lost in final wash waters. Few new mills have been established in this country during the last 15 years; on the other hand, some of the older ones have gone out of existence. The tendency of late years has been to increase the output of the existing mills, rather than build new ones. Some mills, comparatively few, depend on canals, rivers, etc., for water carriage. The question of freight on raw and manufactured material is now one of the chief determining factors of locality, in conjunction with which may be considered the cost for coal and labour.

Arrangement of Mill.—The old-established mills have been altered and added to from time to time, and their general arrangement consequently represents an adaptation to circumstances and an approximation to what it would be if a new mill were laid down, but in all mills newly constructed there is a general principle or ideal plan underlying the arrangement of the plant which is well exemplified in the illustration (Fig. 87) showing an Indian mill designed and built by Messrs. Bertrams, Limited.

The following is a description of the arrangement of this mill. The raw materials (rags and grasses) are taken into the first room of the main building (starting at the bottom of the page). In this room are situated a rag-washer, three rag-cutters, a willow and duster and a hoist; at the further end, in the

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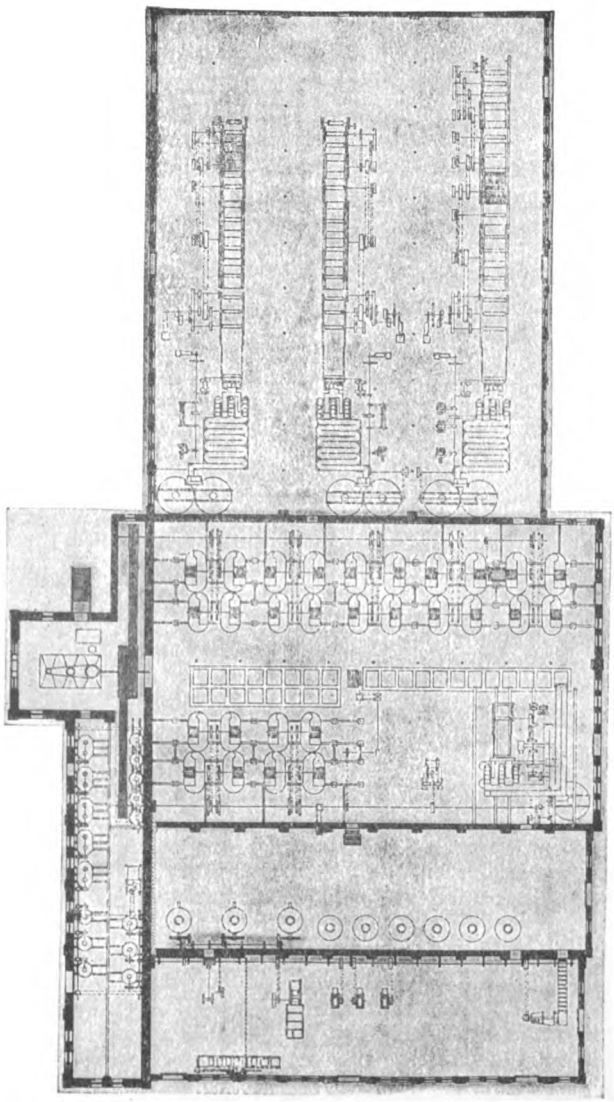

FIG. 87.

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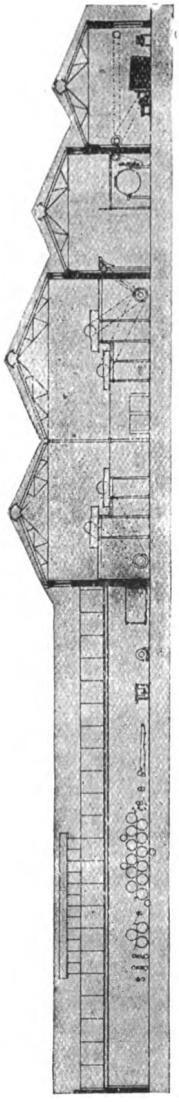

FIG. 88.

portion devoted to the preparation of grass, is a grass duster and elevator. The second room contains three spherical revolving boilers for rags and six stationary boilers for grass. This room is fitted with a stage above the level of the boilers, to which the raw materials are elevated from the first room. In the third room are arranged fourteen washing and breaking engines and fourteen beating engines, the former being placed at a slightly higher elevation than the latter so that the prepared half-stuff can be discharged straight from the breakers to the beaters when such a procedure is followed. Along the middle of this room at the ground level, rows of draining chests are placed into which the material can be discharged for bleaching and subsequent draining. A presse-pâte arrangement is shown in one corner of this room, and the main water pump of the mill is also situated here. The fourth and largest room of the mill is the machine room, containing three Fourdrinier paper machines, one of them being adapted for the manufacture of animal-sized papers. Beyond the machine room in the same line of buildings, but not shown in the illustration for want of space, is a fifth room, the finishing room or 'salle' in which are situated the cutting machines and hydraulic packing presses. In the annexe, shown in the plan (Fig. 87) at the side of the main building, are placed the dissolving vats for the chemicals, lime and caustic soda, and mixing

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vats for bleach and clay. In the same annexe, in a separate room, alongside the beater-room, is placed the main steam engine of the mill from which power is transmitted to all the various departments. The steam-boilers, fitted with economisers, are placed in a separate building near the engine-room, but not shown in the plan. The Porion evaporator for soda recovery is also situated in a separate building near the boilers. The main water tank is placed on the roof of the chemical house annexe.

Underground Water.—In certain districts, notably in the home counties, the available amount of water is running short on account of the excessive pumping occasioned by manufacturers, water companies and others, resulting in the permanent lowering of the water levels, and necessitating the deepening of wells. In such localities it becomes necessary that the paper-maker should study the subject of available supplies with a view to the future. He must also in every way minimise his consumption by using water over again where possible, as with the back water, and re-use of wash waters, etc. Marked economies have been effected in this direction during the last few years, but at some considerable sacrifice. Records of rainfall, percolation, flow of streams and fluctuation of well levels cannot be too strongly insisted upon, as they afford data upon which available supplies can be gauged.

An institution, known as the 'Underground Water Preservation Association,' 15 Borough, largely supported by the paper trade, has instituted simple rules for such measurements and records, from which we make the following abstracts:—

For the measurement of streams take a board of sufficient length and width to dam the stream, cut a notch in the top of the board deep enough to pass all the water to be measured, the length of the notch not to exceed two-thirds of the width of the stream (see Fig. 89).

The bottom and ends of the notch should be bevelled on the down stream to a sharp feather edge perfectly level.

Drive a stake into the bed of the stream three feet back

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from the board, the top being exactly level with the knife edge of the sill, the level may be checked as the water begins to overflow the sill.

The board must be wide enough to set the water at a dead level before it passes the sill, and with large currents, the water should, where possible, have a clear fall of 12 inches below.

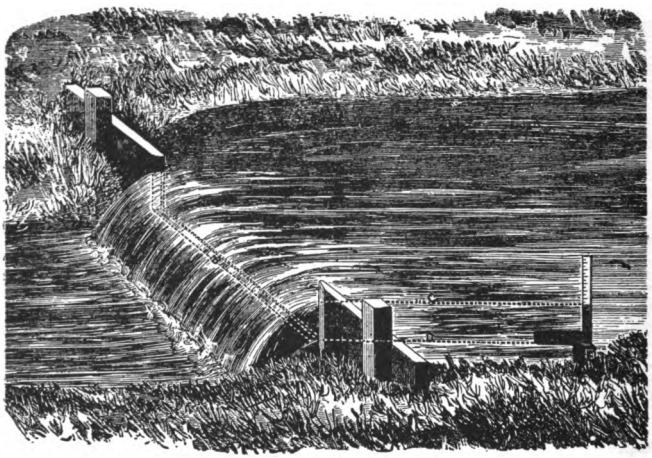

Fig. 89.

Measure the depth of water over the top of the stake by means of a square, or a thin edged rule. This gives the true depth of water over the sill.

The volume of water passing over the sill can be found from the depth measurement without calculation, by reference to Hennell's 'Hydraulic Tables' (E. and F. N. Spon, Limited, 57 Haymarket, 5*s*.).

In measuring wells a definite level should be selected at the top of the well to measure from, such as a sill or floor level, which level should be invariably adhered to.

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Record 1. Ordnance Datum (O.D.) level of sill (if possible).
„ 2. Depth of well (sill to bottom).

The measurements to be taken and entered on body of chart at regular intervals (i.e. weekly, fortnightly, or monthly) are either :—

„ 3. The depth of water in the well, or
„ 4. Level of water below surface, or
„ 5. Ordnance Datum level of water, or

All three simultaneously at the option and convenience of the observer.

No. 1. Record is ascertained by usual method.

No. 2. Record is determined by lowering weight at the end of a tape or cord and measuring length of same.

No. 3. Record is determined as No. 2, and noting length of wetted cord, or may be determined by lowering line or chesterman tape with attached flat lead (3 inch diam. by ½ inch thick) to surface of water. In the former case the depth of water is got at by direct measurement, and in the latter by deducting the distance measured from total depth of well.

No. 5. Record is arrived at by adding depth of water in well to O.D. level of well bottom, or by deducting No. 4 measurement from O.D. sill level. The latter is more accurate, especially if bottom of well is irregular.

No. 4. Record is perhaps of most value to paper-makers, who are more concerned with the depth of water below the surface than with any other form of measurement.

No. 3. Record is useful in seeing how near the level is to bottom of well, and for comparison with fluctuations of rainfall if latter is simultaneously recorded on diagram.

No. 5. Record is of particular use when comparing different levels in same or adjoining localities.

The Association prefer for their own records Nos. 4 and 5.

The Association's chart (Fig. 90) which is self-descriptive, is designed for simultaneously recording the well, stream, and rainfall records or any one of these for the period of one year.

Water Softening.—Water required for steam raising

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has in many cases to be 'softened' to prevent the formation of scale in the boiler. The water used in the actual manufacture of the paper is, however, seldom treated chemically, but where necessary is filtered. The kind of plant that is used in filtration of the incoming water may also be available for treating the effluent.

The soluble impurities of water consist mainly of carbonate and sulphate of calcium and magnesia, together with traces of

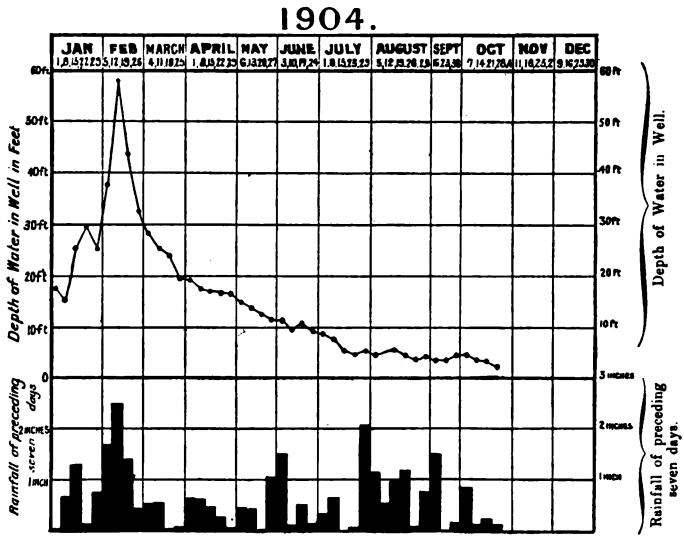

FIG. 90.

iron and organic matter. It is a moot point among paper-makers whether or not the presence of the two former in a water is objectionable. For boiling and bleaching purposes it undoubtedly is, as when mixed with caustic soda or bleaching liquor they form precipitates which line the insides of boilers, breakers, and potchers as a hard scale, which is always liable to become detached, and to find its way into the finished paper, Moreover, carbonates of calcium and magnesia are precipitated

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in the fibre, and carry with them a certain quantity of colouring matter, the subsequent removal of which is difficult.

Carbonate of calcium, though practically insoluble in pure water, is soluble in water containing carbonic acid. When this carbonic acid is neutralised by lime or soda, the carbonate is precipitated. The sulphate of calcium is unacted upon by lime, but by the action of caustic soda is converted into free lime and sodium sulphate. The lime then neutralises the free carbonic acid in the water, and forms carbonate of calcium, which is of course precipitated.

These reactions may be represented by the following equations :—

Calcium bicarbonate.

	Calcium carbonate.		Carbonic acid.		Lime.		Calcium carbonate.
1.	$CaCO_3$	+	CO_2	+	CaO	=	$2\,CaCO_3$

	Calcium sulphate.		Caustic soda.		Calcium hydrate.		Sodium sulphate.
2.	$CaSO_4$	+	$2NaOH$	=	CaH_2O_2	+	Na_2SO_4

	Calcium hydrate.		Carbonic acid.		Calcium carbonate.		Water.
3.	CaH_2O_2	+	CO_2	=	$CaCO_3$	+	H_2O

If sodium carbonate be used instead of caustic soda, the decomposition will take place thus :—

Calcium sulphate.		Sodium. carbonate.		Calcium carbonate.		Sodium sulphate.
$CaSO_4$	+	Na_2CO_3	=	$CaCO_3$	+	Na_2SO_4

It will be seen from the above equation that in the boiling processes the lime salts are removed from the water at the expense of an equivalent quantity of caustic soda. The same thing applies also to the salts of magnesia. The amount thus decomposed is not perhaps sufficiently large to make it advisable on that account to purify the water. It is indeed so small that processes of purification, based upon the use of lime and caustic soda, are now largely used, the cost for chemicals rarely exceeding 1*d.* per 1000 gallons. But for the reasons we have stated above, and also from the fact that it serves to remove

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dissolved iron and organic matter from a water, such a purification process is in certain cases advisable.

The processes now in use consist, as we have indicated, in the addition to the water of lime and caustic soda or carbonate of soda, the quantities being regulated according to the hardness of the water and the relative proportions of the carbonates and sulphates of calcium and magnesia.

Some mills still use the Clark's system of water softening which consists of adding clear lime water to the hard water in sufficient quantity to precipitate the temporary hardness. To this is added sufficient carbonate of soda solution to remove the 'permanent hardness.' The precipitation is slow; the tanks required occupy a large floor space and each mixing has to be properly adjusted. The later Porter-Clark process combines the process of settling and filtration. Those particles which do not separate out are intercepted by a filtering medium.

In the Stanhope process, lime-water, soda solution with the hard water are simultaneously introduced into a vertical tank, where they mix and pass downwards. That sediment which does not settle at the bottom is caught on inclined plates, so that the issuing water is clear.

The Collet-Stanhope water softener and purifier, a modification of the above (Figs. 91 and 92) makes provision, by means of a ball-cock, for the automatic inflow of water exactly equivalent to that which leaves the apparatus.

The plant is completely automatic; the lime is kept in agitation by means of a chain pump, actuated by the inflowing water; the milk of lime and soda solution, when once properly adjusted to suit the composition of the water, can be left going, merely requiring to be charged occasionally with fresh lime and soda.

The above installation is admirably adapted for water of constant composition.

The Reisert Water Softener.—Manufactured by Messrs. Royles, Limited, Irlam, near Manchester, produces a continuous flow of clear lime water by the upward passage of water through lime sludge in a cone-shaped vessel. When the

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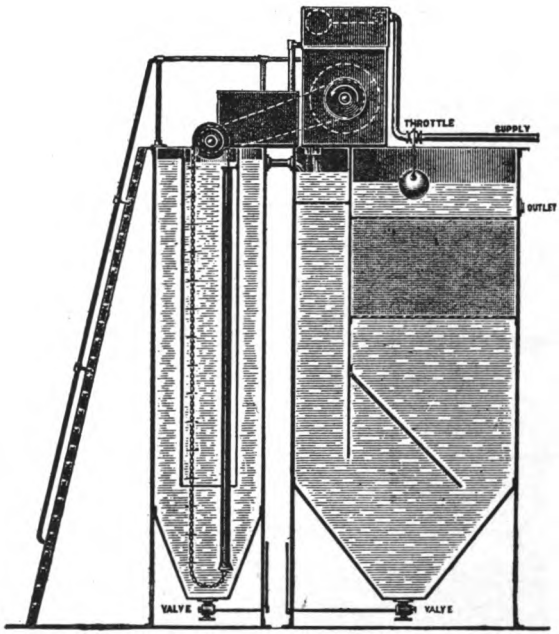
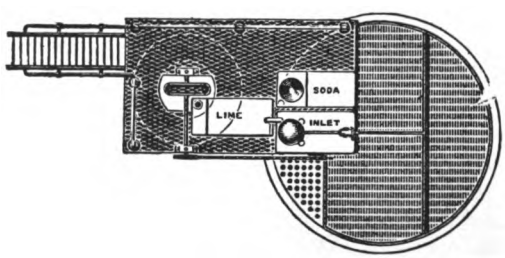
pores of the filter bed become clogged, an automatic flushing is produced by the filling of a syphon, due to the reversal of the direction of the water for a short period.





FIGS. 91 and 92.

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Where waters vary in constituents as is frequently the case from rivers and shallow wells or pumps, and notably in cases where water is drawn from a reservoir containing also more or less condensed or soft water made up in volume with hard water, the Archbutt-Deeley plant (Fig. 93), manufactured by Messrs. Mather and Platt, Limited, of Salford, may, with advantage, be installed. This is an intermittent process. It takes advantage of the well-known principle that, when previously deposited sludge is agitated, complete clarification takes place much more

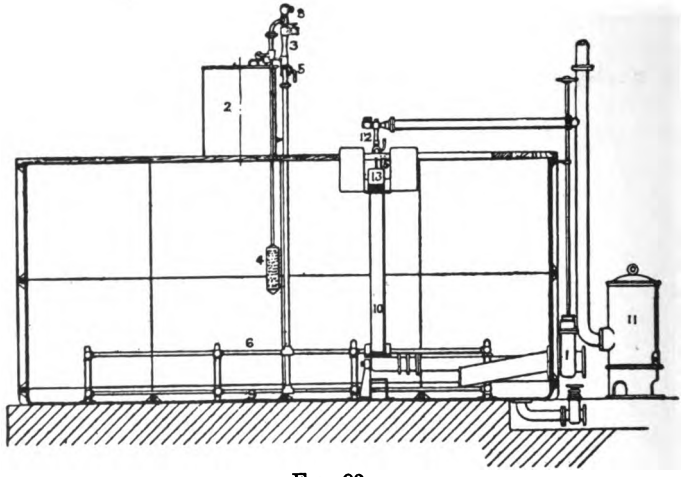

FIG. 93.

rapidly, the heavier particles carrying down the lighter and freshly formed ones.

The *modus operandi* is as follows :—

The hard water is admitted to either tank by means of the supply pipe (1) up to the level of a gauge mark on the side of the tank.

While the tank is filling, the quicklime and carbonate of soda are weighed out, and boiled up with water in the small chemical tank (2) by means of live steam.

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Some waters require also the additional action of an alumina salt, of which the most economical form is the crude sulphate known as 'aluminoferric,' (see p. 358). This is conveniently prepared in the form of a standard solution, of which a measured volume is added to each tank of water immediately after the basic chemicals have been run in.

When the tank is full up to the mark, and the inlet valve has been closed, steam is admitted to the blower (3), causing a current of water to circulate up through the rose (4), the three-way tap (5), down the vertical pipe and back into the tank through the perforations in the upper row of horizontal pipes (6). The three-way tap (7) is then opened and the prepared chemical solution is slowly drawn into the circulating current, and thus diffused throughout the body of water in the tank.

The air-tap (8) is next opened, and air is injected for a few minutes into the water in the tank, through the upper pipes (6); then by reversing the three-way tap (5) the air is forced through the perforations on the under side of the lower row of pipes (9). From these it rises in streams of bubbles, stirring up some of the precipitate or mud, from previous operations, which lies on the bottom of the tank.

After the blower has been in operation for a few minutes (usually ten, but varying with different waters) the steam is turned off, and in about one hour the precipitate will have settled to the bottom of the tank, and the water, even at a depth of six feet from the surface, will not retain on an average more than one part per 100,000 of suspended matter. The efficiency of the treatment can be readily controlled by a few simple tests.

Owing to the relative solubility of the hydrated carbonates of magnesia, waters containing magnesium compounds will retain a certain amount of the carbonate after softening. Under ordinary conditions this is liable to form a deposit in pipes, and especially in the feed apparatus of steam boilers, which may become very troublesome. In order to retain this carbonate in a more permanently soluble form the Archbutt-

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Deely plant is provided with means for re-carbonating the softened water by the injection of carbon dioxide.

The operations of carbonating and drawing off are automatically and simultaneously effected by means of the hinged pipe (10) of rectangular section, the mouth of which is kept just below the surface of the water by means of floats. Fuel gas from the coke stove (11) is forced continuously, by means of the small steam blower (12), up the pipe, escaping by the discharge mouth (13) and being caught by the descending current of water (which in flowing down the pipe is repeatedly splashed upwards by baffles fixed at intervals along the bottom) is carried along with the water through the ball tap (14) fixed over the small supply tank, into which the softened and carbonated water falls, whilst the residual nitrogen, etc., of the fuel gas escapes into the air. If the small tank should fill up and cause the ball tap to close, the gas escapes through the vent pipe (15). A gauge mark on the side of the softening tank, about two feet from the bottom, indicates the level below which the water is not drawn off. Shortly before the water reaches this level the further descent of the discharge pipe is stopped by a 'rest' fixed on the bottom of the tank.

The Criton Water Softener manufactured by the Pulsometer Engineering Company, Limited, consists of vertical tanks arranged to occupy a minimum of floor space. By an ingenious contrivance the hard water is introduced, simultaneously with the lime and soda solutions, into a mixer, from which it passes to the bottom of a vertical tank, rising to the top and passing through an overflow pipe to a filter, and thence to the outlet. The filter is cleansed without the removal of the filtering medium, but merely by opening and closing certain valves. The discharge of the reagents is regulated in accordance with the quantity and composition of the water to be softened.

Filtration of Water Supply and Treatment of Mill Effluent.—Water supply containing matters in suspension is best treated by passing through one or other of the well-known self-cleansing filters among which may be mentioned the following :—

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Wilson's Patent Automatic self-cleaning filter, manufactured by Messrs. Masson and Scott, Limited, of London.

Reeves' Patent Filter, manufactured by Messrs. Mather and Platt, Limited, of Salford.

The Gravity and Pressure Filters (Fig. 94) manufactured by the same makers are largely used for filtration of water supplies to paper-works.

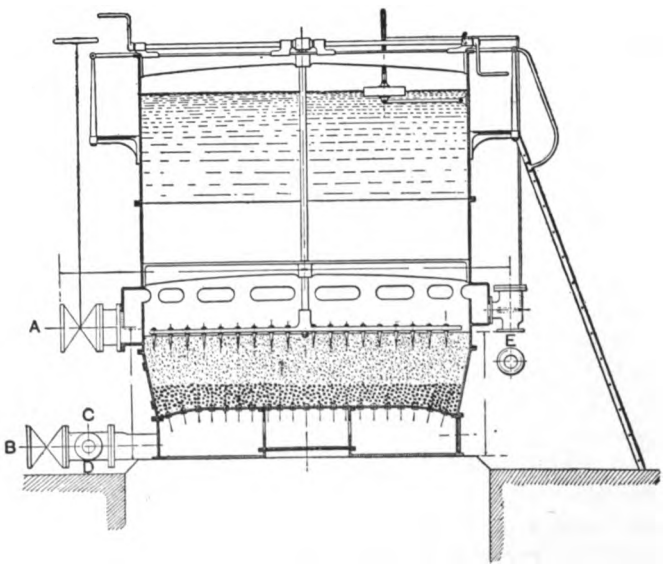

FIG. 94.

When in operation the unfiltered water is admitted through the inlet valve attached to the annular channel, and passing downwards through the quartz bed, by which the impurities are removed, the water is collected by the nozzles in the dished plate into the bottom chamber and emerges in a filtered condition through the outlet valve.

During the cleansing process, the inlet valve for unfiltered water and the outlet valve for filtered water are closed, the wash-

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out inlet valve and wash-out discharge valve being opened. Water is thus admitted into the chamber at the base of the filter and passing up through the quartz bed, whilst the rake is at the same time revolved, carries the accumulated impurities with it into the annular channel, finally escaping through the wash-out discharge valve into any convenient drain or other receptacle.

As soon as the water from the wash-out discharge valve is seen to be clean, this valve and the wash-out inlet valve are closed, and water again admitted through the unfiltered water inlet valve, the rewash valve being at the same time opened for a few moments to allow the first discharge to run to waste, so as to clear the nozzles and collecting chamber of any dirt which may have entered with the wash out water, and to settle the bed into a properly compact condition before restarting the filtering operation.

In our knowledge, one mill is filtering one million gallons per day with these gravity filters, and another three million gallons per day, to be used in the manufacture of their papers.

The Torrent Filter.—Manufactured by the Pulsometer Engineering Company, Limited, contains a layer of suitable filtering material on a grating, under which is a distributing apparatus for air. The cleansing of the filter, which occupies a few minutes about every ten hours, is effected by admitting simultaneously a reverse flow of water with air at a high pressure supplied by a steam blower. This produces a rapid agitation of the particles whereby the dirt and suspended matter are washed away, leaving the filtering material clean to settle down for the next operation.

Effluents from paper works frequently contain flocculent organic matter, albuminoids, etc., both in suspension and dissolved. The best method of dealing with these is by the use of 'aluminoferric,' a product produced by Messrs. Peter Spence and Sons, of Manchester, supplied in slabs, measuring about 21 inches by 12 inches by 5 inches, and weighing about 56 lb. The concentrated alum supplied by Messrs. Pochin and Company, Manchester, is equally efficacious. The above cakes are placed

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either in an iron cage or in a wooden box liberally perforated with ½-inch holes (tapering inwards) in the channel or conduit leading to the settling tanks, so as to insure the water coming freely in contact with them. The aluminoferric is gradually dissolved, fresh cakes being placed in the box as the old ones disappear.

The accompanying drawing (Fig. 95) gives a general idea of the method of using aluminoferric as recommended by

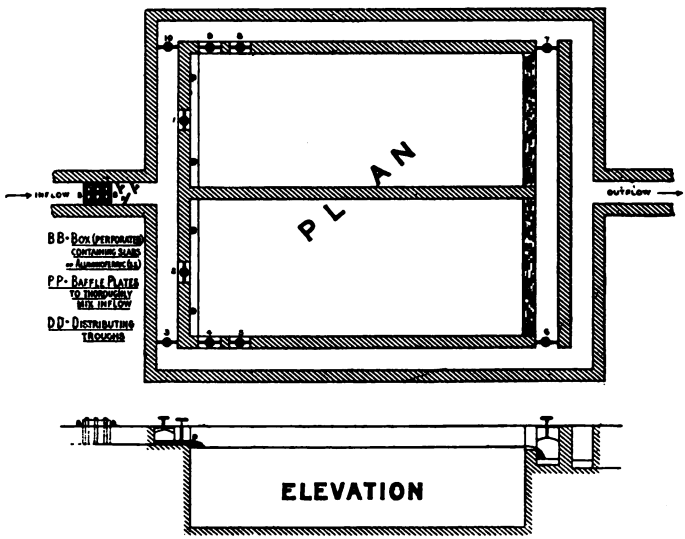

FIG. 95.

Messrs. Spence, also of a system of settling tanks which may with advantage be adopted by manufacturers for purifying their waste water. B B represents the box or cage containing the aluminoferric standing in the channel or conduit.

P P represents a series of baffle plates to insure the aluminoferric being thoroughly mixed before flowing into the tanks.

The two tanks shown may be used in two different

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ways, as may best suit the special circumstances of each manufacturer.

(*a*) They may be used independently by opening 1 and 2, and closing 3 and 10. The treated water will thus pass into both tanks, where precipitation will take place, and, when full, will flow over the sill at the end, and—6 and 7 being open—the clarified water would pass away into the outfall.

(*b*) 2 and 3 and 10 being closed, the treated water will flow into No. 1 tank, and passing forward will overflow into the channel at the end, and—6 and 7 being also closed—the water will flow into No. 2 tank, and —4 and 5 being open—will flow into the side channel and pass away into the outflow as in the first instance. Or, the working as described in *b* may be reversed by closing 1 and 10 and opening 8 and 9.

The quantity of aluminoferric depends, of course, upon the amount of purification to be effected. In some cases a ton will be sufficient to purify a million gallons. In other instances, where the water is highly impure, experience shows that it may be necessary to use the equivalent of two tons per million gallons.

The above mentioned process we have found in particular valuable in the purification of effluents discharged into water-courses where stringent regulations are enforced by the Rivers Commissioners, compelling the manufacturers to keep their effluent to a high degree of purity.

Save-all.—Waste washwaters are sometimes treated for recovery of suspended fibre. This can be done in the most simple manner by allowing the water from the washers to flow into a slowly revolving wire-covered cone-shaped drum on a horizontal axis (see Figs. 53 and 54, p. 246). The washwater enters at the smaller and the pulp discharges at the larger end; the water, deprived of fibres but still containing matter in suspension, passes through. This simple appliance does excellent work, but for dealing with large quantities of such waters and especially machine backwaters containing fine fibres, mineral, starch, etc., in suspension, the Füllner Separator is, perhaps, the most generally employed.

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It consists of a horizontal tank on the cone-shaped bottom of which the particles settle, and from which they are periodically drawn off. It acts furthermore as a reservoir from which water may be drawn for the furnish of the beaters. The suspended particles are drawn off from the bottom.

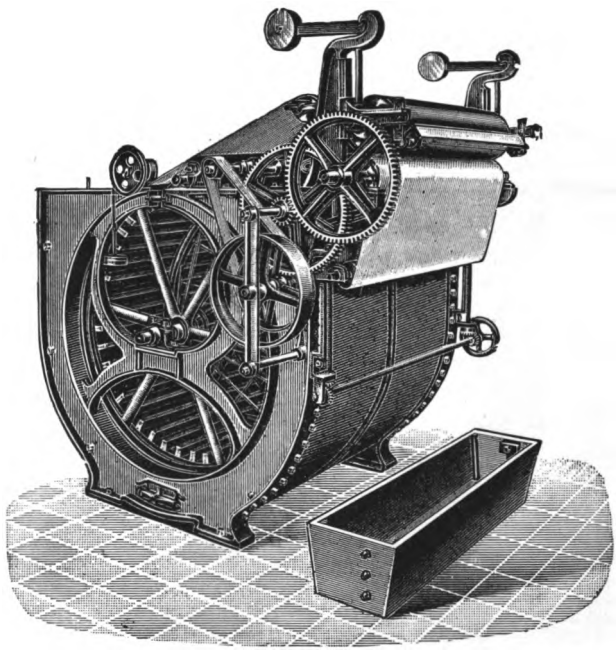

FIG. 96.

The latest improvement in this department of the mill is the Füllner Continuous Rotary Filter * shown in perspective in Fig. 96 and in diagrammatic section in Fig. 97.

It consists of a drum A revolving in a vat B. The periphery of the drum is constructed of wooden bars over which galvanised

* Eng. Patents 19237 and 22852 of 1901.

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iron wire is wound in the form of a right and left-handed spiral starting from the middle. The ends of the drum are quite open and pass through the sides of the vat, leakage being prevented by suitable packing rings. The drum is covered by an endless felt which is kept stretched by the action of the double spiral. The 'backwater' is admitted to the vat outside the drum and the

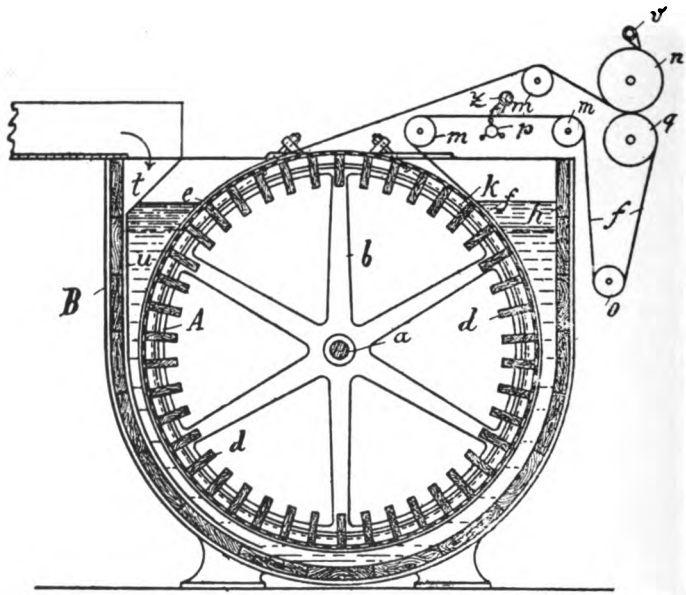

FIG. 97.

solid matters are deposited on the felt whilst the filtered water flows through the felt and is discharged through the ends of drum outside the vat. The solid matters are collected on the felt in the form of a cake, which is carried by the felt to the press-roll *n* which removes the cake, and is itself cleaned by the scraper *v*. The broken cake falls off the roll in a semi-solid state into a box below, and the felt returns to the vat over the

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guide-rolls *o* and *n*, being washed on its way by a spray of water *z*, and a felt-beater *p*. More efficient arrangements for the occasional cleansing of the felt are also provided. The filtering capacity of this machine is said to be from 30,000 to 150,000 gallons in twenty-four hours, and its stuff-recovering capacity from 2 to 6 tons dry weight per week.

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CHAPTER XVI.

SPECIAL MANUFACTURES.

THERE are a number of industrial products which are modified papers, and result from some treatment, mechanical or chemical, applied to the web, either at the stage previous to finishing as paper or in other cases a treatment applied to the finished paper. We briefly describe the more important of these special products.

Pulp Yarns.—It will have been observed in the general discussion of cellulose, that the structural properties of papers merge into those of a textile fabric, also that paper is normally the complement of the textiles, and utilises in its production a unit fibre of such dimensions as lie outside the possibility of twisting or spinning to a continuous yarn. It is true that modern invention has very much extended the limits of textile utility, and systems are in operation for dealing with extremely short lengths of fibre. There is, in fact, an intermediate region between the two great divisions of the cellulose industries, and in this region there have been various recent inventions; in one direction extending the dry processes of the spinner, in the other converting a web produced as paper, i.e. by wet agglomeration into a textile yarn. It may be observed that paper suitably twisted is employed by the Japanese in the place of twine; the paper so used is that made from the Broussonetia, or paper-mulberry, and has exceptional structural characteristics.

Paper or pulp yarns by the newer European processes are of two types; certain inventors merely cut paper into strips of 2–3 mm., and subject these to a rolling process, followed by spinning or twisting. But these products are inferior in textile

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quality to those made by the second group of processes. In these, a web of paper is prepared by the usual method and appliances, but is sub-divided while still in the form of wet web into strips, these strips passing forward through press rolls and being partially dried on cylinders and reeled. In this state they retain sufficient plasticity to yield to a rolling process in which, while passing forward in continuous lengths, they are subject to the action of an alternating pair of rollers at right angles to the direction of travel, which convert the flat strip into the cylindrical. In this form they are finally subjected to a spinning, or rather, twisting treatment, on an ordinary spinning frame. The effects of these treatments on tensile properties is illustrated by the following comparative numbers, the tests being carried out under equal conditions of humidity (45 p.ct.) and temperature (17°).

Description.	Size of Yarn.	Breaking Length.	Extensibility per cent.
1. 'Silvalin' strips, dry . .	2·891	2·390	3·06
2. Finished yarn, from . .	2·900	4·810	6·44
3. Altdamm-Türk strips . .	13·153	4·170	2·84
4. Strips after rolling . . .	8·222	5·014	2·24
5. „ „ „ . .	8·408	5·187	2·71
6. Same strips rolled and twisted .	12·100	6·413	3·06

The processes referred to above are the Altdamm-Türk representing the consolidated system embodying the patents of Kellner, Türk, and later patents of the Altdamm Company. The 'Silvalin' product is made by the patents of Kron. These inventions have been worked since 1891, and are the subject of a series of patents of various inventors, but these appear to have taken final form in the two products above-mentioned.

For a full account of this new industry, students may consult an excellent monograph entitled 'Papierstoffgarne' (Zellstoffgarne, Xyolin, Silvalin, Licella), by Prof. E. Pfuhl (Staatsrath). Riga, 1904.

Hydrated Cellulose.—In treating of the property of cellu-

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lose we have pointed out that the fibres are transformed into structureless, gelatinous, and therefore still colloidal masses, under the action (1) of continuous milling with water, as in the beating engine (p. 178). (2) More extreme actions are determined by solvents of cellulose, which attack fibrous celluloses to form colloidal solutions. In these solutions, the cellulose is present as a derivative or combined with the reagent employed, but reversion to cellulose is determined in many cases by a simple dilution with water. Industries based upon this transformation of cellulose have been established for many years. The best known is the application of the cuprammonium solvents in the production of 'Willesden' goods. Of this industry we give the following brief account.

The action of a solution of copper oxide in ammonia upon cellulose has been already referred to (see p. 9). Celluloses, and also certain ligno-celluloses, when treated with such a solution, gradually gelatinise and finally dissolve. On evaporating the solution to dryness, a gummy amorphous mass is obtained, containing the cellulose intermixed with copper oxide.

If the cellulose be in excess, e. g. when the solution is evaporated on the surface of paper, calico, etc., merely dipped in the solution, free copper oxide is often not formed at all, but a green varnish-like mass of cellulose combined with copper oxide, which coats the surface of each filament, welding and cementing them together. This cement-like *cupro-cellulose*, as it may be termed, being insoluble in water communicates water-resisting properties to the material so treated : moreover, the presence of copper renders the fabric less prone than before to be attacked by insects and mould, so that animal and vegetable life of a parasitic nature and fungoid growths are rarely, if ever, to be observed, even when the material is kpet under conditions where boring worms, ants, rot and mould, would be likely to attack it.

As has been already indicated (p. 9), the solution of cuprammonium hydroxide is preferable to one containing cuprammonium salts ; not only is the action on cellulose more energetic, but various other advantages are obtained.

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Preparation of the Copper Solution.—The cuprammonium solution is prepared according to the patent of Dr. C. R. Alder Wright (No. 737, 1883).

A series of cast-iron towers, two to three feet in diameter and ten to twelve feet high, is so arranged that a current of air can be blown by a powerful engine successively through the whole series. The towers are then nearly filled with fragments of metallic copper (crumpled up sheet, cuttings, etc.), and solution of ammonia; the air-current being turned on, oxidation of the copper and solution of the oxide so produced are rapidly effected.

The ammonia solution employed is previously impregnated with a considerable quantity of copper by passing a stream of water over scrap copper in similar towers, a current of ammonia gas mixed with a suitable proportion of air being at the same time forced in. The liquor passing from one tower is used over again to supply a second instead of water, and so on through the series: finally the liquor is brought up to full copper strength in the series of towers described above.

The spent air issuing from the towers carries with it a notable quantity of ammonia; this is intercepted by means of an 'exhaust' scrubber containing copper, and well supplied with water, whereby a comparatively weak solution of ammonia and copper is obtained, which can be used instead of water in the first series of towers.

In order to produce the maximum effect on the cellulose, the solution should contain from 100 to 150 lb. of ammonia, and from 20 to 25 lb. of copper per 100 gallons.

By decomposing a cuprammonium solution by means of metallic zinc, a corresponding solution of zinc-ammonium hydroxide can be obtained. This solution is also capable of gelatinising cellulose, but not to the same extent as the copper solution. It may, however, be advantageously employed in certain cases in conjunction with a copper solution. Such a solution can be conveniently prepared by substituting brass for copper in the dissolving-towers. It is worthy of note that although, as we have seen, zinc has the power of replacing

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copper in a cuprammonium solution, iron is without any action, although it readily replaces copper in a solution of copper sulphate. This fact is of very great industrial importance, as it enables the manufacturer to employ vessels and machinery of iron.

The 'Willesden' goods may be divided into two classes. Goods of the first class, such as rope, cordage, netting, etc., are prepared by simply dipping the made-up materials in a bath of cuprammonium solution, using certain precautions as to the mode of immersion and its duration, and the strength of the solution. On subsequently drying the dipped fabrics, they are obtained coated and impregnated with cupro-cellulose, which thus not only forms a kind of varnish-like surface dressing, but further adds strength to the fibres by more or less intimately cementing them together.

Goods of the second class constitute a much more important group to which at present the Willesden Company more especially devotes its attention. These fabrics are essentially of three kinds, viz., Willesden Canvas, Willesden Scrim, and Willesden Paper. The two former of these classes are prepared in much the same way as the goods just described, saving that the fabric to be treated is usually unwound from one roller and rewound upon another, after passing through the bath and over a succession of drying cylinders.

Willesden Paper.—This may be divided into two departments, viz. (1) Willesden unwelded; (2) Willesden welded, the first class being prepared from a single web of paper by passing it through the bath, rolling and drying. Certain coarse varieties furnish a waterproof material excellently adapted for lining packages, etc. Finer qualities furnish envelopes and stationery, possessing the valuable property of not being affected by water. Letters written on such paper would remain perfectly legible, even after prolonged immersion. It may be interesting to point out here that the cuprammonium solution offers a very simple means of fastening envelopes in such a way as to be proof against any attempts at tampering. The method consists in using a concentrated solution as the fastening material; the envelope is

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then closed and ironed with a warm flat-iron, whereby the gelatinised cellulose is converted into an insoluble cupro-cellulose, and the cover is fastened so securely that the only possible mode of opening is by tearing the paper.

Willesden Welded Goods are prepared by simultaneously dipping two or more sheets of paper and pressing them into one compact homogeneous sheet whilst the surfaces are still in a gelatinous state. In this way a continuous length of fabric of extraordinary durability is produced that is scarcely affected by water, even when heated in it for some weeks at a pressure of 60 lb. per square inch.

As, on drying fabrics treated with cuprammonium solution, the whole of the ammonia in the solution absorbed by them is volatilised, it is necessary, in order to make the process economical to collect and re-use this ammonia. This is effected by conducting the drying process in closed chambers, from which the ammonia gas is conducted by suitable appliances and recovered.

In addition to the advantages already mentioned, it may be stated that Willesden paper is much less inflammable than ordinary paper.

Among the many uses to which Willesden goods can be applied, the following may be cited: Roofs and sheds; huts and tents; partitions; tanks and pipes; damp-proof foundations; underlining slates; sails, awnings, etc.

Vegetable Parchmentising.—The action of sulphuric acid upon cellulose may be also controlled to produce the valuable product known as Vegetable Parchment, a pure cellulose paper (water-leaf) is passed through a bath of sulphuric acid, varying between the limits of 53°–60° B., corresponding with 67·0 to 78·1 p.ct. sulphuric acid strength. The web of paper, after passing through the acid, is immediately plunged into water which arrests the action of the acid, and determines the fixation of the reverted cellulose now as a semi-fibrous colloidal aggregate. The web requires to be exhaustively washed to remove the last traces of acid, and is then dried on drying cylinders. Previously to the drying, it is treated in a bath of glycerine and glucose, which has the effect of preventing the brittleness which

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would otherwise result from the total drying of the product. Up to the year 1880, this process was carried out by an interrupted method, which has now, however, largely given place to an entirely continuous process, based on the original patents of R. Fritsch. A number of technical data have to be taken into account in working these processes, of which the more important are :—

The preparation of the original webs of paper. In making these for the thicker sorts, the stuff is very rapidly beaten, so that the paper has a maximum of absorbency. For papers of less substance, 30–45 grms. per square metre, the preparation of the stuff in the beater involves 2–3 hours working, as, to compensate for less substance, the web requires to be more resistant, to stand the tensions in the acid bath. The rag celluloses are employed as raw material. In the acid bath there is a shrinkage of the web of paper (1–2 p.ct.) ; on the drying cylinders, this shrinkage is much more pronounced, and reaches 12–13 p.ct. in the width of the web. To regulate and control these shrinkages, so as to retain an even surface and a flat sheet, of course, requires very careful adjustment of the subsidiary mechanical appliances.

The zinc chloride solvents of cellulose are also used to attack cellulose, and convert it into a colloidal semi-fibrous mass. When in this state, various sheets or webs may be rolled or compacted together so as to give dense boards of very considerable tensile strength. After producing the fabric in crude form, it requires extensive washing to remove finally all soluble by-products.

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CHAPTER XVII.

STATISTICS.

THE statistical study of paper-making may be extended by the specialist to very wide limits, covering all numerical returns concerning raw materials, as well as the production, distribution, and consumption of paper. Of these, certain only may be regarded as indispensable to the paper-maker, viz.: (1) *Special*, which are the numerical returns for individual mills showing the expenditure in quantities and values for the aggregate or unit of output of finished paper. (2) *General*, comprising such figures as the Board of Trade returns for the trade of the United Kingdom in raw materials and finished papers.

Special.—Classified returns of the workings of a paper-mill and its several departments are just as necessary for the full control of the manufacture as are the 'account books' with the periodical balance-sheet, for the proper working of the 'business' of the mill. Such returns fall obviously under the main heads of raw materials, labour, chemicals, and steam. The further subdivision of the returns will take into account the various sections or departments of the mill; thus, the 'boiling' or half-stuff plant; bleaching, beating and machines will be separately dealt with. In an esparto mill, there will be special returns for the soda recovery plant, and in a sulphite mill for the liquor-making plant. The returns for boilers and steam raising will be recorded in a book showing the total consumption of coal and water for steam per diem, or per week, from which the evaporative efficiency is calculated and recorded. From time to time careful boiler trials should be conducted. The combustion of coal in the furnaces can be controlled by analysis of the flue gases duly recorded for reference.

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The purpose of these returns is obviously to secure 'efficiency and economy' in all departments of the mill, to indicate all sources of waste or 'leakage,' and what is of course very important to provide a statement of cost of every kind and quality of paper turned out. Such considerations are generally recognised and need not be further insisted on. There is, however, an aspect of statistical returns which is too often lost sight of, and that is that they provide permanent records of manufacturing experience. Such records have a practical usefulness in two directions, they provide against bad work, and for progressive improvement based upon continual observation of effects.

In regard to the planning and carrying out of an adequate system of statistics and records, only general instructions can be given. From the point of view of the business, the one purpose is to arrive at costs per pound or per ton for each of the innumerable qualities produced, from that of the manufacture, the purpose is to give an account of every pound of material taken into work in terms of final manufactured products, and as regards quality to refer the various items of quality of papers to the conditions obtaining in their production.

The latter order of statistics are those with which we are mainly concerned; they are the more comprehensive and include such returns from which actual money costs are calculated. We venture to think that the careful study of the preceding chapters of this work will supply the main outlines of a scheme of returns required, in any particular case. The knowledge, which we have endeavoured to convey is based upon quantities and measurements; and that knowledge in practice implies the continued quantitative study of all the processes of the mill, as well as of the raw materials and finished papers. To take as an example the treatment of esparto: the following quantitative observations may be made.

Loss on dusting, yield of half-stuff, including yield of fibre from boilers after washing, and from potchers or presse-pâte after bleaching; proportion of caustic used in boiling; amount of dilution in boilers by condensation of steam; proportion of soda recovered; fuel required for recovery; proportion of bleaching

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liquor used in potchers, and the amount of residual bleaching 'chlorine'; all losses at the various stages. At the beaters, every item of the 'furnish' is carefully controlled, together with the agents used in antichloring, sizing, and colouring. On the machine, in addition to a return of its turn-off in finished paper observations are made upon the back water to determine fibre, loading, sizing, and colouring constituents passing away unfixed by the wet web of paper. Lastly, the physical constants of the finished paper, which, in connection with records of all the previous treatments, gives a complete history of all makes for quality.

Books showing the life of machine wires, wet and dry felts, are carefully kept in mills. Such books should show in addition to maker's name, price, gauge, hours of working, also amount of paper produced, so that the cost per ton for such renewals can be calculated upon each ton of paper made. Such times as the amount of water consumed at different stages with due allowance for that which is used over again, should not be neglected, and, furthermore, the paper-maker should know exactly what it costs him per 1000 gallons, to raise his water from well to cistern, including other charges. The coal consumption per ton of paper should be recorded each week and for different qualities where possible. The cost per indicated horse-power for his different engines should be periodically recorded and indicator diagrams taken for the purpose. And lastly the costs of beating, including power, renewal of bars, etc., should be estimated and entered.

It is unnecessary to prosecute this subject into minute detail. We repeat in conclusion that the paper-maker is only a 'technologist' in his art, when his experience issues in the practice of precise records, and his control of a mill is based upon these essential statistics of production.

General.—Statistics of this kind are of indefinite extent, and for the purpose of the student we are limiting ourselves to such numerical returns as show the leading lines of distribution and evolution of the manufacture.

We are particularly indebted for much of this matter to the work of A. Dykes Spicer in course of publication (Methuen

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and Company). This work is of an exhaustive character and readers may be referred thereto for fuller information.

Historical.—The following abstract of statistics will convey an impression of the progress of the manufacture in this country and the United States. We begin from the year 1850 and in the special figures relating to esparto and wood pulp, it will be remembered that the introduction of these materials represent periods in the evolution of the manufactures with particular reference to our own country.

1850.

Paper mills in	England	327
„ „	Scotland	51
„ „	Ireland	37
		415

Number of machines employed in United Kingdom 412, with 344 vats.

Paper charged excise duty in the United Kingdom, 141,032,474 lb.; 7,762,686 lb. were exported.

Great Britain imported 8124 tons rags, of which, 32 tons come from United States, and 23 tons from Egypt.

United States imported 20,696,875 lb. rags at 3.61 cents per lb., of which 15,861,266 lb. came from Italy and Austria.

Total value of imported rags $748,707.

Paper imported valued at $496,563.

1851.—Paper manufactured in United Kingdom, 150,903,543 lb., of which, 8,305,590 lb. were exported. There were 413 machines, and 330 vats in the United Kingdom.

United States imported rags to the value of $903,747 at 3.46 cents per lb. Export of paper from United States $155,664.

1852.—Paper manufactured in United Kingdom, 154,469,211 lb. valued at £2,000,000, of which was exported 7,328,886 lb.

United States exported paper value amounting to $119,535. Export of rags from England this year amounted to 2462 tons.

United States imported rags to amount of 18,288,458 lb. at

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3.46 cents a lb. amounting to $626,729, of which 12,220,570 lb. came from Italy.

1853.—Rags imported into the United States were valued at $982,837. The quantity was 22,766,000 lb. at 4.31 cents. per lb. 2,666,000 lb. were obtained from England, and Italy sent 14,171,292 lb.

Export paper United States to value of $122,212.

Import rags Great Britain this year and two preceding averaged yearly 9332 tons.

Paper manufactured in England amounted to 66,000 tons yearly.

Paper manufactured in Great Britain and Ireland was 177,633,010 lb., of which 13,296,874 lb. exported.

1854.—Rags annually consumed in Great Britain and France combined 436,800,000 lb. producing 291,200,000 lb. paper, 4·55 lb. per capita. Per capita in United States 10·80.

Paper manufactured in Great Britain chargeable with excise duty was 179,896,222 lb.; increase of 100,000,000 lb. in 20 years.

Exports were 16,122,202 lb. Value of paper manufactured £2,000,000.

750 mills in United States.

3000 engines producing 250,000,000 lb. paper at 10 cents a lb. Requiring 405,000,000 lb. rags at 4 cents a lb. Cost of labour and stock nearly $20,000,000. Cost of manufacture—$27,000,000 worth of paper estimated at $23,625,000.

Annual consumption of rags in Great Britain 120,000 tons.

Paper imports in United States $727,829.

Price of rags in England :—

1st	quality	32*s*. to 34*s*.	per cwt.
2nd	„	20*s*.	„
3rd	„	15*s*.	„
4th	„	10*s*.	„

Exports from United States said to have been $187,325 and books and maps $191,843.

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Quantity of rags imported into United States 32,615,753 lb. Value $1,010,443 at 3.09 cents a lb.

1855.—Rise of ½*d.* a pound in price of paper in England — affected journals.

United States imported 40,013,516 lb. rags, of which 23,948,612 from Italy. Value $1,235,515 at 3.06 cents a lb. Improvements in machinery and the application of steam reduced the number of mills in the United Kingdom to 380, or nearly one half in 20 years, during which time the amount of rags annually consumed was 201,600,000 lb.

1856.—Consumption of paper in the United States equalled France and England together.

1857.—Paper manufactured in Great Britain 191,000,000 lb.

Rags imported into United States 44,582,080 lb. valued at $1,448,125.

1858.—There was a decrease of 6,000,000 lb. in quantity of paper charged with duty in Great Britain in the year ending June 30 as against 1857, the relative quantities being 99,483,635 lb. in 1857, and 93,462,130 lb. in 1858.

1859.—Quantity of paper charged with duty in British Kingdom was 217,827,192 lb. Exports 20,142,350 lb.

1860.—In United States 65 p.ct. of paper stock derived from domestic rags of cotton, 12 p.ct. from cotton waste.

$5,000,000 worth of paper consumed per annum in New York. England required 120,000 tons rags yearly.

Commons repealed duty established by Queen Anne.

1861.—Excise and import duty on paper in England abolished.

1864.—Of the 271 mills in United Kingdom 211 paper-making companies petitioned Parliament for abatement of taxes and all restrictions abroad upon exports.

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TABLE FROM THE PARLIAMENTARY RETURN, 1850–1859, SHOWING DUTY CHARGED, DRAWBACK AND HOME CONSUMPTION OF PAPER.

Year.	Charged with Duty.	Exported on Drawback or free of Duty.	Returned for Home Consumption.
	lb.	lb.	lb.
1850	141,032,474	7,762,686	133,269,788
1851	150,903,543	8,305,598	142,597,945
1852	154,469,211	7,328,886	147,140,325
1853	177,633,010	13,296,874	164,336,135
1854	177,896,224	16,112,020	161,784,204
1855	166,776,394	11,118,551	155,657,843
1856	187,716,575	14,798,979	172,917,596
1857	191,721,620	16,031,063	175,690,557
1858	192,847,825	16,548,828	176,298,997
1859	217,827,197	20,142,350	197,684,847

Esparto.—The year 1860 witnessed the introduction of this important staple: the subjoined table shows the growth and fluctuations of the consumption.

TOTAL QUANTITY AND VALUE OF ESPARTO IMPORTED INTO THE UNITED KINGDOM FOR MAKING PAPER FROM 1861 (THE FIRST YEAR OF RECORD AT THE CUSTOM HOUSE) TO 1905 INCLUSIVE. (Summarised from Messrs. Ide and Christie's Market Returns.)

Year.	Quantity in tons.	Value, £	Year.	Quantity in Tons.	Value, £
1861	16	88	1884	184,005	1,125,553
1862	876	4,042	1885	201,036	1,149,434
1863	19,326	77,306	1886	195,151	999,258
1864	43,403	212,494	1887	200,116	962,049
1865	52,324	272,827	1888	248,836	1,270,324
1866	70,041	312,819	1889	217,256	1,090,266
1867	55,074	260,581	1890	217,028	1,045,722
1868	95,880	615,914	1891	212,666	1,033,998
1869	87,422	523,582	1892	212,967	1,029,901
1870	104,870	761,521	1893	185,450	870,431
1871	144,411	1,239,181	1894	184,960	819,265
1872	104,621	803,396	1895	186,408	791,236
1873	102,649	843,672	1896	187,278	796,683
1874	119,176	972,393	1897	204,579	825,195
1875	141,900	1,113,285	1898	197,341	768,779

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TOTAL QUANTITY AND VALUE OF ESPARTO IMPORTED—*cont.*

Year.	Quantity in tons.	Value, £	Year.	Quantity in tons.	Value, £
1876	130,891	1,046,449	1899	207,604	806,354
1877	175,878	1,286,237	1900	200,280	800,498
1878	140,505	932,300	1901	193,937	802,463
1879	161,971	1,055,616	1902	198,292	717,854
1880	191,229	1,372,573	1903	179,089	649,501
1881	192,493	1,286,211	1904	200,245	746,489
1882	180,849	1,281,105	1905	191,114	724,552
1883	206,762	1,386,297	1906		

IMPORTATION OF ESPARTO FOR MAKING PAPER TO UNITED KINGDOM IN 1905.

As regards the countries of origin, the following are the figures for 1905 :—

	Tons.	Value £
From Spain	42,741	217,560
„ Africa	84,813	290,955
„ Tunis	26,720	92,123
„ Tripoli	36,760	123,663
Other countries	80	351
	191,114	£724,552

Wood-Pulp.—Wood cellulose, or chemical wood-pulp, began to be produced industrially in the period 1870–1880. The following are the particulars of imports.

BRITISH IMPORTS OF WOOD-PULP.

(Compiled from returns published in 'The Paper Trade Review.')

The first year that wood-pulp imports were separately classified was in 1887 :—

IMPORTS.

	Tons.	£		Tons.	£
1887	79,543	511,450	1897	388,304	1,939,761
1888	110,040	677,866	1898	404,842	1,894,395
1889	121,534	688,571	1899	415,113	1,989,703
1890	137,837	766,841	1900	487,742	2,617,789
1891	156,609	851,389	1901	448,455	2,406,084
1892	190,946	981,025	1902	525,799	2,398,215
1893	215,920	1,184,265	1903	576,153	2,506,583
1894	279,765	1,432,400	1904	568,901	2,519,077
1895	297,095	1,574,302	1905	578,012	2,759,627
1896	327,080	1,684,647	1906		

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In 1898 and 1899 the import figures were classified to show the arrivals of both chemical and mechanical wood-pulps as under :—

	Chemical.		Mechanical.	
	tons	£	tons	£
1898	179,525	1,226,093	225,317	668,302
1899	196,926	1,441,806	281,187	547,897

In 1900 the total figures only were shown. Commencing from 1901 the imports, both of chemical and mechanical, dry and wet, are given :—

Chemical.

	Dry.		Moist.	
	tons	£	tons	£
1901	172,801	1,518,042	15,146	87,830
1902	185,443	1,507,555	13,161	65,204
1903	211,823	1,642,082	21,279	82,012
1904	211,372	1,667,394	24,785	91,413
1905	231,374	1,919,962	18,094	72,903
1906				

Mechanical.

	Dry.		Moist.	
	tons	£	tons	£
1901	13,309	96,817	246,199	703,395
1902	11,103	66,280	316,022	759,176
1903	6,263	30,192	336,788	752,297
1904	9,199	40,845	323,869	721,197
1905	10,267	46,924	318,277	719,838

The imports for the first half of the present year show a total 270,960 tons, of the value of 1,281,020*l.*, made up as follows :—

	tons	£
Chemical, dry	103,132	882,186
,, wet	10,694	43,459
Mechanical, dry	3,830	16,382
,, wet	152,604	338,993

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Classified Raw materials.—The imports of raw materials during the last decade are given in the following official returns of the Board of Trade: 'An Account of the Registered Quantities and Values of each kind of Paper-making Materials imported into the United Kingdom during each year from 1887 to 1898 inclusive.'

Years.	Linen and Cotton Rags.		Esparto and other Vegetable Fibres.		Pulp of Wood.		Other Materials and Pulp of Rags.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
	tons.	£	tons.	£	tons.	£	tons.	£
1887	38,273	466,167	200,116	962,049	79,533	511,367	60,120	332,669
1888	41,459	471,566	248,836	1,270,324	110,369	681,173	68,947	367,290
1889	42,443	426,322	217,256	1,090,266	122,179	690,692	46,282	306,537
1890	34,889	354,306	217,028	1,045,722	137,837	766,841	48,398	295,186
1891	32,824	317,555	212,666	1,033,938	156,609	851,389	37,099	258,668
1892	23,032	214,065	212,967	1,029,901	190,946	981,025	26,367	216,314
1893	20,758	199,155	185,450	870,431	215,920	1,184,265	30,358	231,119
1894	20,931	192,314	184,960	819,265	279,765	1,432,400	34,662	265,118
1895	25,033	229,645	186,408	791,236	297,095	1,574,302	25,058	181,713
1896	21,055	206,772	187,278	796,683	327,080	1,684,647	24,106	149,634
1897	25,333	249,631	204,579	825,195	388,304	1,939,761	20,326	135,653
*1898	20,859	193,803	197,341	768,779	404,827	1,894,328	..	..

The most striking features of these figures are: (1) the large relative increase of wood-pulp, with corresponding increase in value; (2) the comparatively steady trade in esparto and rags, accompanied, however, by a falling off in values, which in the case of rags is conspicuously large.

Since the wood-pulps rank as 'half-stuff,' it is clear that the main tendency of the paper manufacture of the United Kingdom is to increase in the direction of working up such half-stuff, and abandoning the chemical treatment of raw materials.

* In this year the Board of Trade initiated a classified return of wood-pulps, and the gross amount as given in the table was made up of *mechanical pulps*, 225,317 tons (value 668,302*l.*), and *chemical pulps*, 1,791,510 tons (value 1,226,026*l.*). Of the former, about 60 per cent. is imported from Scandinavia; of chemical pulps, the Scandinavian countries contribute about one-half.

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The corresponding returns for the period 1901 to 1905 are as below :—

TOTAL QUANTITIES AND VALUES OF FOREIGN AND COLONIAL PAPER-MAKING MATERIALS *imported* 1901 TO 1905.

——	1901.	1902.	1903.	1904.	1905.	1901.	1902.	1903.	1904.	1905.
	tons	tons.	tons.	tons.	tons.	£	£	£	£	£
Linen and cotton rags.	15,922	18,942	22,051	22,186	23,681	146,703	173,732	194,319	196,016	224,232
Esparto, and other vegetable fibres for making paper . .	193,937	198,292	179,089	200,245	191,114	802,463	717,854	649,501	746,489	724,552
Pulp of wood :										
Chemical, dry . .	173,801	185,443	211,823	211,392	231,374	1,518,042	1,507,555	1,642,082	1,667,558	1,919,962
„ wet . .	15,146	13,161	21,279	24,785	18,094	87,830	65,204	82,012	91,448	72,903
Mechanical, dry . .	13,309	11,103	6,263	9,199	10,267	96,817	66,280	30,192	40,845	46,924
„ wet .	246,199	316,092	336,788	323,869	318,277	703,395	759,176	752,297	721,197	719,838
Other materials . .	16,446	14,656	12,410	12,795	13,502	98,056	96,972	81,064	906580	94,090
Total of paper-making materials	674,760	757,689	789,703	804,471	806,309	3,453,306	3,386,773	3,431,467	3,554,133	3,802,501

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Chemicals.—It will be of interest to note the variation in prices of more important chemicals used by the paper-maker, which we are able to give from the year 1871 to the present, and for these figures we are indebted to Messrs. W. Royse and Co., of Albert Square, Manchester.

Year.	Bleach, 35 to 37 per cent.	White, 70 per cent.	Ammonia Alkali, 58 per cent.	Flowers.	Sulphur Recovered.	Alum. Lump.	Sulphate of Alumina.
	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
1871	12 0 0	..	..	..	..	6 0 0	..
1872	14 14 0	..	..	..	..	8 0 0	..
1873	11 15 0	..	..	..	..	8 12 6	..
1874	9 5 0	..	..	..	..	8 7 6	..
1875	7 13 3	..	..	..	..	7 10 0	5 18 3
1876	6 1 3	..	..	..	..	6 17 6	4 16 3
1877	5 10 9	..	..	..	..	6 13 4	4 6 0
1878	4 13 2	11 13 3	..	..	..	6 0 0	3 18 9
1879	5 5 0	10 18 6	..	9 13 9	..	6 3 6	3 6 3
1880	5 6 9	10 15 0	..	10 2 6	..	6 7 6	3 5 0
1881	4 6 3	10 5 6	..	10 15 0	..	5 16 9	3 5 0
1882	3 18 9	9 6 3	6 10 9	11 3 9	..	5 15 0	2 16 3
1883	7 6 9	9 12 6	6 15 0	11 0 0	5 12 6	5 14 6	2 14 6
1884	5 3 9	9 16 9	6 7 6	10 18 9	5 11 3	5 11 3	4 17 6
1885	6 5 6	8 13 3	1¼d. per degree	10 17 6	5 6 9	5 10 0	4 18 6
1886	6 8 9	8 4 3	1 1/16 d. ,,	9 0 0	4 18 0	5 10 0	4 7 3
1887	7 10 0	7 11 3	4 17 6 per ton	9 3 9	3 11 3	5 3 0	4 10 0
1888	7 8 0	6 18 9	4 11 3	8 10 9	4 14 3	5 0 0	3 18 9
1889	5 17 6	6 14 6	4 16 3	8 17 6	5 2 6	5 0 0	4 10 0
1890	6 0 0	10 11 9	6 12 6	8 1 3	4 8 0	4 17 6	5 5 0
1891	6 18 0	10 12 6	6 6 9	10 0 0	6 11 3	5 0 0	5 2 6
1892	8 1 9	10 3 9	6 1 9	9 1 3	4 19 3	5 0 0	5 0 0
1893	8 3 9	9 12 6	4 12 0	8 7 6	4 1 9	4 18 9	4 8 9
1894	7 8 3	8 11 9	3 5 6	7 13 9	3 17 6	4 18 0	3 18 9
1895	7 0 0	7 9 3	3 3 9	6 18 9	3 15 0	4 11 3	4 0 0
1866	6 13 9	7 3 9	3 7 6	7 11 3	4 3 0	4 12 6	4 0 0
1897	6 2 6	7 0 0	3 18 0	8 0 0	4 13 9	4 11 3	4 0 0
1898	5 0 0	6 18 3	4 0 0	8 0 0	4 10 0	4 10 0	4 0 0
1899	5 1 3	7 13 9	4 5 0	8 0 0	4 10 0	4 10 0	4 0 0
1900	6 12 6	10 2 6	4 10 0	8 0 0	4 11 3	4 10 0	4 0 0
1901	6 16 3	10 2 6	4 17 6	7 5 0	4 12 6	5 0 0	4 0 0
1902	6 3 9	9 12 6	4 17 6	7 12 6	4 14 6	5 0 0	4 0 0
1903	3 17 6	9 12 6	4 10 0	7 8 9	4 15 0	5 2 6	4 6 0
1904	4 8 9	9 12 6	4 10 0	7 10 0	4 15 0	5 5 0	4 10 0
1905	4 7 6	9 12 6	4 10 0	7 10 0	4 15 0	5 5 0	4 10 0
1906	4 10 0	9 12 6	4 10 0	7 5 0	4 15 0	5 10 0	4 10 0

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Paper.— The imports of manufactured paper for the period 1901 to 1905, are given in the following :—

TOTAL QUANTITIES AND VALUES OF FOREIGN AND COLONIAL PAPER-MAKING MATERIALS *imported* 1901 TO 1905.

—	1901.	1902.	1903.	1904.	1905.	1901.	1902.	1903.	1904.	1905.
Paper:	cwt.	cwt.	cwt.	cwt.	cwt.	£	£	£	£	£
Unprinted on reels	3,654,090	1,147,463	1,313,847	1,433,668	1,681,387	2,965,606	739,316	837,284	920,989	1,043,145
Ditto, not on reels		2,575,918	2,803,360	3,007,259	3,187,812		2,300,299	2,404,250	2,541,576	2,601,742
Printed paper hangings	136,350	171,939	171,993	167,477	48,363	421,911	545,514	554,640	511,661	133,118
Other printed or coated papers					161,059					436,860
Strawboard or millboard	2,029,962	2,019,661	2,355,646	2,115,039	..	736,857	695,642	775,593	695,471	..
Strawboard	..	..	..	..	1,803,706	..	..	..	..	543,728
Millboard and wood-pulp board	..	..	..	..	1,178,564	..	..	..	..	497,472
Wood-pulp board	460,905	555,970	613,850	627,097	..	217,860	256,903	278,416	270,922	..
Total of paper	6,281,307	6,470,951	7,258,696	7,350,540	8,061,341	4,342,234	4,537,674	4,850,183	4,940,619	5,256,065

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Contrast with the imports, the following table of paper, etc., manufactured in the United Kingdom, and exported for the same period.

TOTAL QUANTITIES AND VALUES OF FOREIGN AND COLONIAL PAPER-MAKING MATERIALS *exported* 1901 TO 1905.

—	1901.	1902.	1903.	1904.	1905.	1901.	1902.	1903.	1904.	1905.
Paper:	cwt.	cwt.	cwt.	cwt.	cwt.	£	£	£	£	£
Writing or printing, and envelopes . .	716,857	761,322	823,773	891,222	962,202	1,095,278	1,122,289	1,224,923	1,251,652	1,286,388
Hangings	69,337	74,185	75,845	81,683	84,225	194,801	194,018	206,472	204,241	208,861
Pasteboard, millboard, cardboard, and cards (including playing cards)	41,885	37,715	47,727	53,961	62,508	75,083	68,579	78,740	89,092	96,274
Bags	27,428	27,910	28,537	29,309	33,516	27,557	27,486	30,338	30,947	35,581
Unenumerated and articles of paper (except bags)	192,746	180,691	170,616	204,026	202,442	275,858	260,332	255,377	300,865	312,663
Total of paper. .	1,048,253	1,081,823	1,146,498	1,260,201	1,344,853	1,668,577	1,672,704	1,795,850	1,876,797	1,939,767

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In reference to the distribution of manufactures in this country, the following classification of production will be of interest. It represents the results of very careful computation from statistics for the year 1895 :—

Brown	20
Grey (wrappings)	23
Printings (news)	16
,, (fine)	21
Writing	20
	100

It is interesting to note that these five main classes of papers are produced in approximately equal tonnage.

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CHAPTER XVIII.

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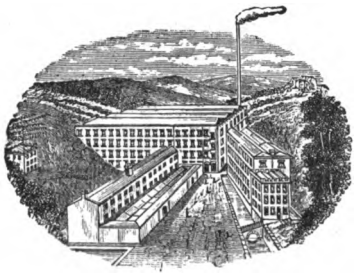

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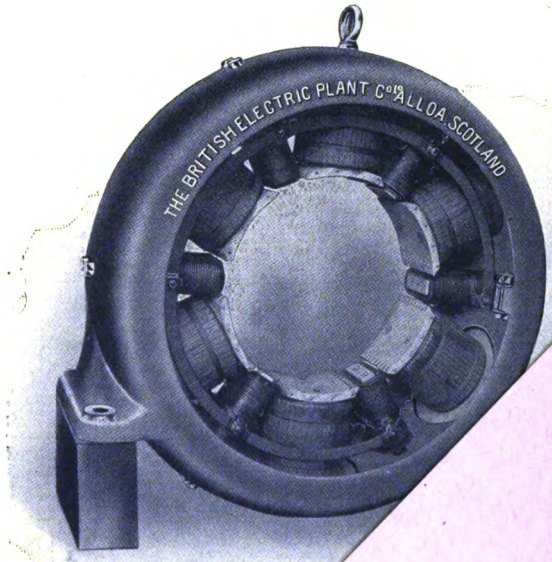

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